Fraternal Twin Hemicage Chelates

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Supporting Information

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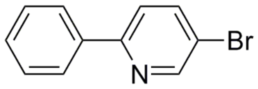
Experimental section

General

Commercial chemicals were used as supplied. All reactions were performed using standard Schlenck techniques under inert (N_2) atmosphere. Flash column chromatography was performed using silica gel (Silia-P from Silicycle, 60 Å, 40-63μm). Analytical thin layer chromatography (TLC) was performed with glass backings (250 μm with indicator F-254). Compounds were visualized under UV light. GCMS samples were separated on a Shimadzu HP5-MS 30 m x 0.25 mm ID x 0.25 μm film thickness column. ^{1}H and ^{13}C NMR spectra were recorded on either of the following spectrometers: a Brucker Avance at 300 MHz and 75 MHz, respectively; a Varian INOVA at 400 MHz and 100 MHz, respectively; a Varian INOVA at 600MHz and 150 MHz, respectively. COSY and NOESY were recorded on a Varian INOVA spectrometer at 400 MHz or Varian INOVA spectrometer at 600MHz. DQCOSY, HMBC$_{H\text{-}C}$ were recorded on a Varian INOVA spectrometer at 600MHz for ^{1}H and 150 MHz for ^{13}C. The following abbreviations have been used for multiplicity assignments: “s” for singlet, “d” for doublet, “t” for triplet, “m” for multiplet, and “br” for broad. Deuterated cholorform ($CDCl_3$) was used as the solvent of record except where noted below. Melting points (mp’s) were recorded using open end capillaries on a Meltemp melting point apparatus and are corrected. High and low resolution mass spectra were recorded with a VG Micromass ZAB-2F spectrometer. All reaction solvents were dried through Pure Solv^{TM} solvent purification system.

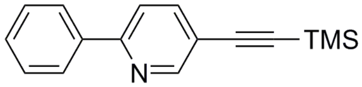
fac-Ir(ppy)$_3$ **(1)**

To a suspention of 2-phenylpyridine (101 mg, 0.65 mmol, 3.1 equiv.) in ethylene glycol (7.5 mL) was added Ir(acac)$_3$ (102 mg, 0.21 mmol, 1.0 equiv.). The mixture was degassed twice and heated at 250°C, for 67 h. The reaction was poured into H_2O/DCM (1:1, 100 mL). The phases were separated and the aqueous phase was extract with DCM (6 x 25 mL). The organic phases were combined and dried over $MgSO_4$. The organic phase was filtered and then concentrated under reduced pressure. The crude was purified by flash chromatography (20% Et_2O/Hexanes on silica, and recrystalized in DCM/Hexanes to obtain 104 mg as a yellow solid (75 %). Rf : 0.56 (50% hexanes/DCM). The ^{1}H NMR spectrum corresponds to that found in the literature.[1]



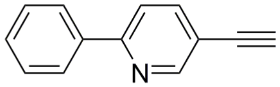
(GSTP-C1-054-01) **5-bromo-2-phenylpyridine (2)**

To a solution of bromobenzene (6.99 mL, 66.4 mmol, 1.05 equiv.) in THF (75 mL) at -78°C was added *n*-BuLi (2.5 M in hexanes, 28 mL, 69.6 mmol, 1.1 equiv.) over 0.25 h. The mixture was stirred for 0.25 h at -78°C, then a solution of $ZnCl_2$ (9.49 g, 69.6 mmol, 1.1 equiv.) in THF (75 mL) was canulated over 0.10 h. The flask was washed twice with THF (10 mL). The mixture was heated at room temperature and stirred for 2.50 h. The zincate solution was canulated to a mixture of 2,5-dibromopyridine (15.0 g, 63.3 mmol, 1.0 equiv.) and Pd(PPh$_3$)$_4$ (3.65 mg, 3.16 mmol, 0.05 equiv.) in THF (80 mL). The flask was washed twice with THF (10 mL). The reaction mixture is heated to reflux for 16 h. The reaction was followed by GCMS and 100% conversion was observed. The mixture was cooled to room temperature. To the solution was added an aqueous solution of EDTA:NaHCO$_{3(sat)}$ (1:1, 150 mL) and stirred for 1 h at 0°C. A white precipitate was formed and was filtered out on to Celite© and washed with THF. The solvent was concentrated under reduced pressure then in vacuo. The aqueous phase was extracted with DCM (3 x 100 mL). The organic phases were combined and washed with a solution of EDTA:NaHCO$_{3(sat)}$ (1:1, 5 x 100 mL). The organic phase was dried over $MgSO_4$ and concentrated under reduced pressure then in vacuo. The residue was purified by flash chromatography (10% EtOAc/hexanes on silica) to yield 14.8 g as a white solid (>99%, mp.: 68-71°C; lit[2] mp: 65-66°C). Rf (5% EtOAc/hexanes) : 0.21. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.74 (d, J = 2.2 Hz, 1H), 7.96 (dd, J = 8.0, 1.5 Hz, 2H), 7.88 (dd, J = 8.5, 2.4 Hz, 1H), 7.63 (d, J = 8.4 Hz, 1H), 7.40–7.50 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 156.0, 150.8, 139.4, 138.2, 129.5, 129.0 (2C), 126.9 (2C), 121.8, 119.4. LRMS : 235. HRMS : calculated = 232.9840; found = 232.9834. The ^{1}H NMR spectrum corresponds to that found in the literature.[3]



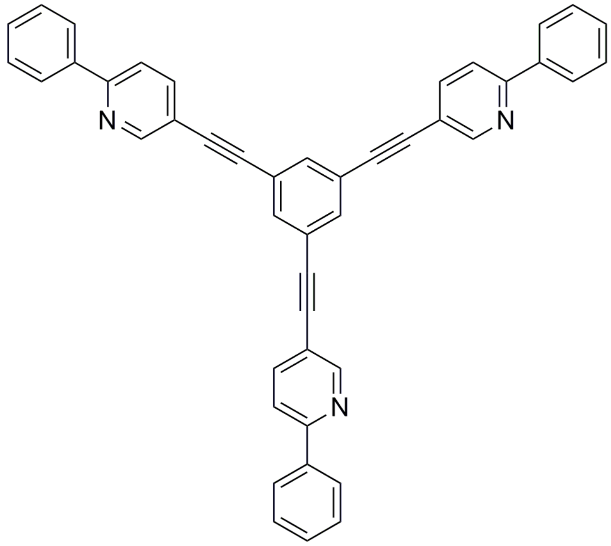
(GSTP-C1-143-02) **2-phenyl-5-(2-(trimethylsilyl)ethynyl)pyridine (3)**

To a solution of **2** (3.5 g, 14.9 mmol, 1.0 equiv.) in THF (150 mL) and *i*-Pr_2NH (50 mL) was added trimethylacethylene (TMSA) (5 mL, 35.4 mmol, 2.4 equiv.), $Pd(PPh_3)_4$ (1.0 g, 0.894 mmol, 0.06 equiv.) and CuI (453 mg, 2.38 mmol, 0.16 equiv.). The solution was degassed and stirred for 18 h at room temperature. The oxidative insertion step was followed by GCMS and 93% conversion was observed. To the reaction mixture was added TMSA (0.5 mL, 3.5 mmol). The solution mixture was degassed and stirred for 4 h at room temperature. The oxidative insertion step was followed by GCMS and 100% conversion was observed. The solvent was evaporated under reduced pressure. The residue was purified by flash chromatography (5-10% EtOAc/hexanes on silica) to yield 3.0 g of light yellow oil (82%). Rf (5% EtOAc/hexanes) : 0.22. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.76 (s, 1H), 8.00 (dd, J = 8.1, 1.2 Hz, 2H), 7.80 (d, J = 8.2, 1.9 Hz, 1H), 7.68 (d, J = 8.2 Hz, 1H), 7.35–7.55 (m, 3H), 0.20 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 156.4, 152.7, 139.7, 138.7, 129.5, 128.9 (2C), 127.1 (2C), 119.7, 118.6 101.9, 98.7, 0.0 (3C). LRMS : 251. HRMS : calculated = 251.1130; found = 251.1135.



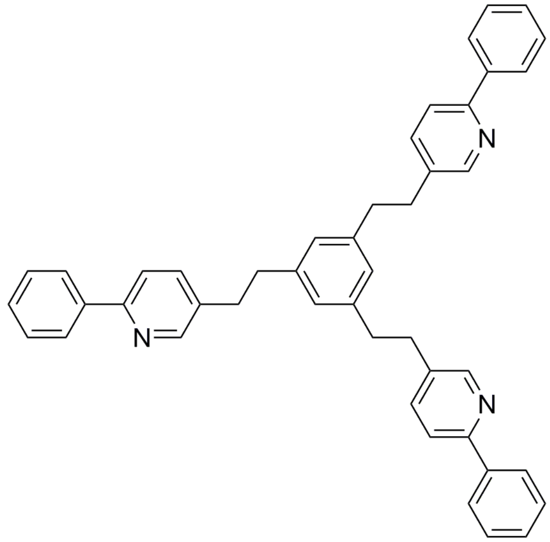
(GSTP-C1-147) **5-ethynyl-2-phenylpyridine (4)**

To a solution of **3** (577 mg, 2.29 mmol, 1.0 equiv.) in MeOH (8 mL) was added K_2CO_3 (728 mg, 5.27 mmol, 2.3 equiv.). The reaction was stirred for 0.5 h. at room temperature. The reaction was followed by GCMS and 100% conversion was observed. The reaction was poured into a solution of H_2O/Et_2O (1:1, 30 mL). The layers were separated and the organic phase was washed with H_2O (2 x 15 mL) and with brine (1 x 15 mL). The combined aqueous fractions were reextracted with Et_2O (3 x 25 mL). The organic phase were combined and dried over $MgSO_4$. The organic phase was filtered and then concentrated under reduced pressure to yield 411 mg of a light yellow solid (>99%, mp.: 39-41°C). Rf (10% EtOAc/hexanes) : 0.43. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.80 (dd, J = 2.1, 0.7 Hz, 1H), 8.00 (d, J = 8.1 Hz, 2H), 7.83 (dd, J = 8.2, 2.1 Hz, 1H), 7.70 (dd, J = 8.2, 0.8 Hz, 1H), 7.35–7.55 (m, 3H), 3.27 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 156.9, 152.8, 139.9, 138.6, 129.6, 129.0, 127.1, 119.8, 117.6, 81.0, 80.8. LRMS : 179. HRMS : calculated = 179.0735; found = 179.0736.



(GSTP-C1-153) **1,3,5-tris((6-phenylpyridin-3-yl)ethynyl)benzene (6)**

To a solution of 1,3,5-tribromobenzene (739 mg, 2.347 mmol, 1.0 equiv.) in Et_3N/Toluene (1:1, 23 mL) was added $Pd(PPh_3)_4$ (263 mg, 0.227 mmol, 0.097 equiv.), CuI (35 mg, 0.188 mmol, 0.08 equiv.) and **4** (1.68 g, 9.390 mmol, 4.0 equiv.). The reaction mixture was degassed 3 times at room temperature with N_2. The mixture was heated to 80^oC for 16 h. The reaction was followed by TLC. The reaction mixture was filtered through a Celite© plug and washed with 10% EtOAc/DCM until no more eluted product was detected. The filtrate was concentrated under reduce pressure. The residue was purified by flash chromatography (2.5/22.5/75 to 5/20/75 EtOAc/hexanes/DCM on silica) to yield 1.25 g of a yellow solid (89%, mp.: $175\text{-}180^oC$). Rf (30% hexanes/DCM: 0.06. ^1H NMR (300 MHz, $CDCl_3$): δ 8.85 (d, J = 1.8 Hz, 3H), 8.03 (dd, J = 8.1, 1.3 Hz, 6H), 7.88 (dd, J = 8.2, 2.1 Hz, 3H), 7.76 (d, J = 8.2 Hz, 3H), 7.76 (s, 3H), 7.35-7.60 (m, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 156.7, 152.4, 139.4, 138.6, 134.6, 129.6, 129.0 (2C), 127.1 (2C), 123.9, 119.9,118.2, 91.2, 88.0. LRMS : 609. HRMS : calculated = 609.2205; found = 609.2192.

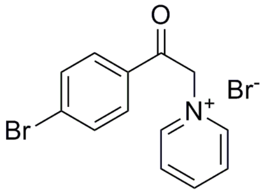


(GSTP-C1-168) **1,3,5-tris(2-(6-phenylpyridin-3-yl)ethyl)benzene (HC1)**

To a solution of **6** (112 mg, 0.184 mmol, 1.0 equiv.) in THF (12 mL) was added Pd/C (20 mg). The mixture was degassed once with N_2 and three times with H_2. The reaction was stirred for 20 h at room temperature under an H_2 atmosphere. The reaction was followed by ^{1}H NMR, the spectrum contained many unsaturated intermediates. The reaction mixture was filtered through a Celite© plug and washed with THF/DCM (1:1). The solvent was evaporated under reduced pressure. The residue was diluted in THF (12 mL) and Pd/C (20 mg) was added. The reaction mixture was stirred for 48 h at room temperature under an H_2 atmosphere. The reaction was followed by ^{1}H NMR, the spectrum showed 100% conversion. The reaction mixture was filtered through a Celite© plug and washed with THF/DCM (1:1). The solvent was evaporated under reduced pressure. The residue was purified by flash chromatography (5 to 20% EtOAc/DCM) to yield 105 mg of a colorless oil (91%). Rf (20% EtOAc/hexanes) : 0.06. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 8.45 (s, 3H), 7.99 (dd, J = 7.0, 1.6 Hz, 6H), 7.65 (d, J = 8.1 Hz, 3H), 7.30-7.60 (m, 12H), 6.82 (s, 3H), 2.85-2.90 (m, 12H). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 8.45 (s br, 3H), 7.99 (dd, J = 7.0, 1.6 Hz, 6H), 7.65 (d, J = 8.1 Hz, 3H), 7.35-7.50 (m, 12H), 6.82 (s, 3H), 2.89 (s br, 12H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 155.3, 150.3, 141.7, 139.7, 136.1, 129.2 (3H), 127.3, 127.1 (2C), 120.4, 37.8, 31.1. LRMS : 621. HRMS : calculated = 621.3144; found = 621.3147.

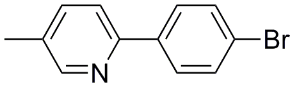
(GSTP-C1-164) **[8 = Ir•HC1]**

To a suspention of **HC1** (150 mg, 0.241 mmol, 1.0 equiv.) in ethylene glycol (24 mL) was added $Ir(acac)_3$ (118 mg, 0.241 mmol, 1.0 equiv.). The mixture was degassed twice and heated to 250°C for 24 h. The reaction was followed by TLC. The reaction was poured into H_2O/DCM (1:1, 50 mL). The phases were separated and the aqueous phase was extract with DCM (5 x 25 mL). The organic phases were combined and dried over $MgSO_4$. The organic phase was filtered and then concentrated under reduced pressure. The crude was purified by flash chromatography (30% hexanes/DCM on silica) to yield 53 mg of a yellow solid (27%, mp.: >350°C). Rf (30% hexanes/DCM) : 0.15. ^{1}H NMR (600 MHz, CD_2Cl_2): δ 7.80 (d, J = 8.2 Hz, 3H), 7.59 (d, J = 7.9 Hz, 3H), 7.52 (dd, J = 8.3, 2.0 Hz, 3H), 6.70-6.90 (m, 9H), 6.57 (s, 3H), 6.38 (d, J = 1.6 Hz, 3H), 3.14 (dt, J = 13.4, 3.0 Hz, 3H), 2.89 (dt, J = 12.6, 3.3 Hz, 3H), 2.54 (td, J = 13.1, 3.2 Hz, 3H), 2.43 (dt, J = 13.4, 3.0 Hz, 3H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 164.4, 161.0, 147.9, 144.5, 140.7, 137.5, 137.0, 135.4, 129.8, 128.4, 124.1, 120.1, 119.2, 38.1, 34.2. LRMS : 811. HRMS : calculated = 811.2538; found = 811.2541.



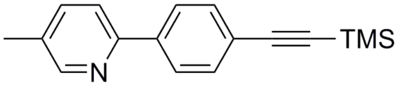
(GSTP-C1-075) **1-(2-(4-bromophenyl)-2-oxoethyl)pyridinium bromide (9)**

To pyridine (16 mL) was added 2-bromo-1-(4-bromophenyl)ethanone (**8**). The reaction was stirred for 0.25 h. A white solid was form as fast as **8** was added. The mixture was filtered on Buckner and washed with Et_2O (4 x 20 mL). The solid was dried on the pump 16 h to yield 5.0 g of a white solid (98%, dec. 243°C, lit[4] mp: dec. 243°C). ^{1}H NMR (300 MHz, MeCN-d_3): δ 8.76 (d, J = 6.1 Hz, 2H), 8.62 (dd, J = 7.9, 7.9 Hz, 1H), 8.12 (dd, J = 7.1, 7.1 Hz, 2H), 7.98 (d, J = 8.6 Hz, 2H), 7.82 (d, J = 8.6 Hz, 2H).



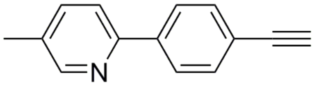
(GSTP-C1-142) **2-(4-bromophenyl)-5-methylpyridine (10)**

To a solution of **9** (4.0 g, 11.2 mmol, 1.0 equiv.) in MeOH (30 mL) was added NH_4OAc (4.3 g, 56.0 mmol, 5.0 equiv.). The mixture was degassed 3 times and methacrolein (930 µL, 11.2 mmol, 1.0 equiv.) was added and the mixture was degassed once more with N_2. The mixture was heated to reflux for 16 h. The reaction was followed by TLC. The reaction was cooled and poured into water (60 mL) and extracted with hexane (5 x 50 mL). The organic phases were combined and dried over $MgSO_4$. The organic phase was filtered and then concentrated under reduced pressure to yield 2.37 g of a light yellow solid (85%, mp.: 99-103^{o}C). Rf (10% EtOAc/hexanes: 0.38. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.51 (s br, 1H), 7.85 (d, J = 8.5 Hz, 2H), 7.50–7.60 (m, 4H), 2.37 (s, 3H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 153.6, 150.3, 138.4, 137.5, 132.1, 131.9 (2C), 128.3 (2C), 123.1, 119.9, 18.3. LRMS : 247. HRMS : calculated = 246.9997; found = 247.0000. The ^{1}H NMR spectrum corresponds to that found in the literature.[5]



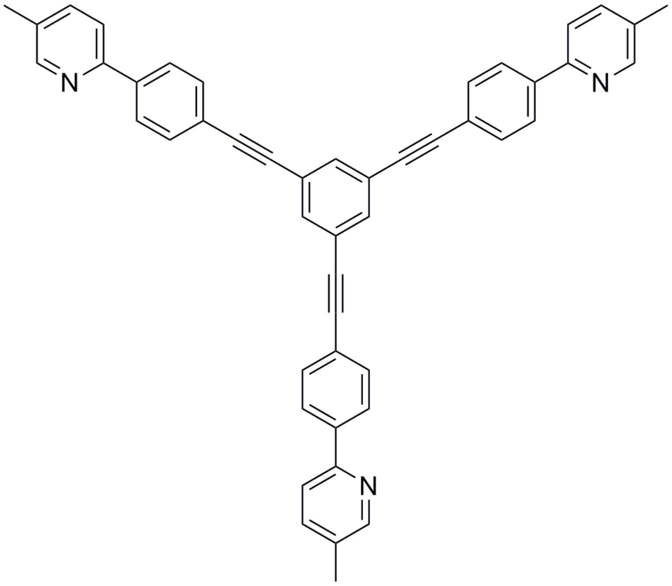
(GSTP-C1-146) **5-methyl-2-(4-((trimethylsilyl)ethynyl)phenyl)pyridine (11)**

To a solution of **10** (2.2 g, 8.87 mmol, 1.0 equiv.) in Et_3N/Tol (1:1, 30 mL) was added $Pd(PPh_3)_4$ (990 mg, 0.861 mmol, 0.097 equiv.), CuI (135 mg, 0.709 mmol, 0.08 equiv.). The mixture was degassed 3 times, TMSA (1.8 mL, 13.3 mmol, 1.5 equiv.) was added and the solution was degassed once more. The mixture was heated to reflux for 16 h. The reaction was followed by TLC. The cold mixture was filtered through a plug of silica and evaporated under reduced pressure. The residue was purified by flash chromatography (5% EtOAc/hexanes on silica) to yield 2.03 g of a brownish solid (86%, mp.: 109-110^{o}C). Rf (10% EtOAc/hexanes): 0.47. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.52 (s br, 1H), 7.93 (d, J = 8.3 Hz, 2H), 7.50–7.70 (m, 4H), 2.38 (s, 3H), 0.27 (s, 9H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 153.9, 150.2, 139.3, 137.4, 132.4 (2C), 132.1, 126.5 (2C), 123.3, 120.1, 105.1, 95.4, 18.3, 0.1 (3C). LRMS : 265. HRMS : calculated = 265.1287; found = 265.1289.



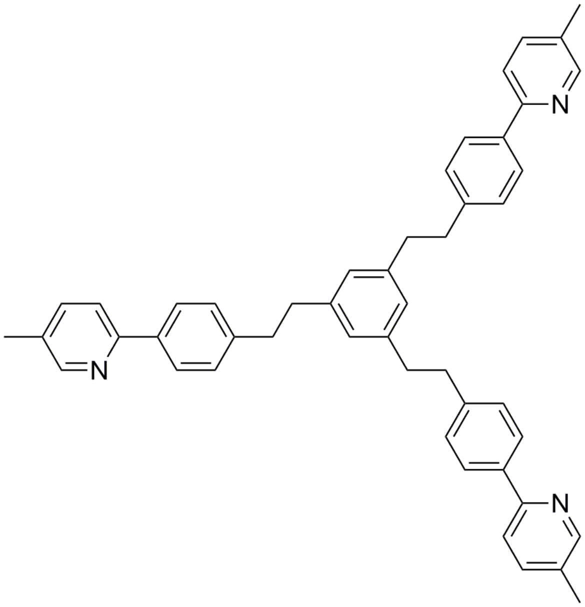
(GSTP-C1-148) **2-(4-ethynylphenyl)-5-methylpyridine (12)**

To a solution of **11** (1.9 g, 7.16 mmol, 1.0 equiv.) in MeOH (25 mL) was added K_2CO_3 (2.3 g, 16.5 mmol, 2.3 equiv.). The reaction was stirred for 0.5 h. at room temperature. The reaction was followed by GCMS and 100% conversion was observed. The reaction was poured into a solution of H_2O/Et_2O (1:1, 50 mL). The layers were separated and the organic phase was washed with H_2O (2 x 30 mL) and with brine (1 x 30 mL). The combined aqueous phases were reextracted with Et_2O (3 x 40 mL). The organic phase was dried over $MgSO_4$. The organic phase was filtered and then concentrated under reduced pressure to yield 1.38 g of a light yellow solid (>99%, 86-88^{o}C). Rf (10% EtOAc/hexanes): 0.26. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.52 (s br, 1H), 7.94 (d, J = 8.3 Hz, 2H), 7.50–7.70 (m, 4H), 3.15 (s, 1H), 2.38 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.8, 150.3, 139.8, 137.5, 132.6 (2C), 132.2, 126.6 (2C), 122.3, 120.2, 83.7, 78.3, 18.3. LRMS : 193. HRMS : calculated = 193.0891; found = 193.0892.



(GSTP-C1-150) **1,3,5-tris((4-(5-methylpyridin-2-yl)phenyl)ethynyl)benzene (13)**

To a solution of 1,3,5-tribromobenzene (560 mg, 1.78 mmol, 1.0 equiv.) in Et_3N/Toluene (1:1, 18 mL) was added $Pd(PPh_3)_4$ (200 mg, 0.173 mmol, 0.097 equiv.), CuI (27 mg, 0.142 mmol, 0.08 equiv.) and **12** (1.38 g, 7.14 mmol, 4.0 equiv.). The reaction mixture was degassed 3 times at room temperature with N_2. The mixture was heated to 80°C for 16 h. The reaction was followed by TLC. The reaction mixture was filtered through a Celite© plug and washed with 40% EtOAc/DCM until no more eluted product was detected. The filtrate was concentrated under reduced pression. The residue was purified by flash chromatography (10% hexanes/DCM) to yield 980 mg of a light yellow solid (85%, mp.: 256-250°C). Rf (30% hexanes/DCM): 0.13. ^1H NMR (400 MHz, $CDCl_3$): δ 8.54 (s br, 3H), 8.00 (d, J = 8.4 Hz, 6H), 7.70 (s, 3H), 7.67 (s br, 3H), 7.64 (d, J = 8.5, 2H), 7.58 (dd, J = 8.1, 1.7 Hz, 3H), 2.39 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.9, 150.4, 139.6, 137.5, 134.2, 132.2 (2C), 126.7 (2C), 124.2, 90.7, 89.0, 18.4. LRMS : 651. HRMS : calculated = 651.2674; found = 651.2678.



(GSTP-C1-168) **1,3,5-tris(4-(5-methylpyridin-2-yl)phenethyl)benzene (14 = HC2)**

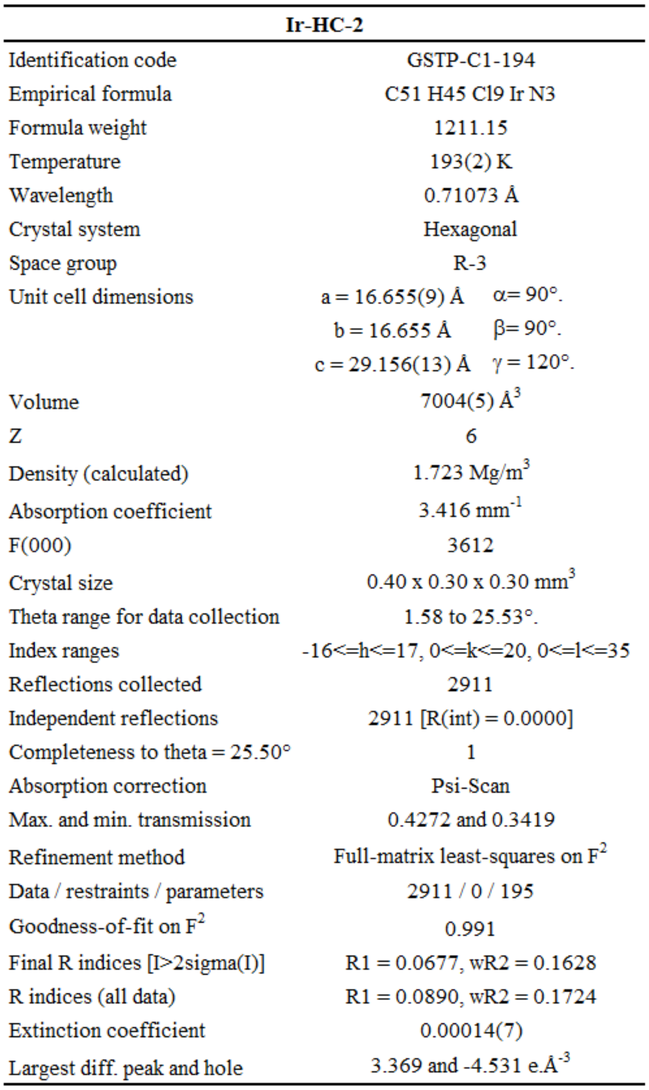
To a solution of **13** (500 mg, 0.767 mmol, 1.0 equiv.) in THF (50 mL) was added Pd/C (100 mg). The mixture was degassed once with N_2 and three times with H_2. The reaction was stirred for 20 h at room temperature under an H_2 atmosphere. The reaction was followed by ^{1}H NMR, the spectrum contained many unsaturated intermediates. The reaction mixture was filtered through a Celite© plug and washed with THF/DCM (1:1). The solvent was evaporated under reduced presure. The residue was diluted in THF (50 mL) and Pd/C (100 mg) was added. The reaction mixture was stirred for 48 h at room temperature under an H_2 atmosphere. The reaction was followed by ^{1}H NMR, the spectrum shows 100% conversion. The reaction mixture was filtered through a Celite© plug and washed with THF/DCM (1:1). The solvent was evaporated under reduced pressure to yield 456 mg of a white solid (89%, mp.: 113-116°C). Rf(10 EtOAc/hexanes): 0.40. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 8.49 (d, J = 2.1 Hz, 3H), 7.91 (d, J = 8.3 Hz, 6H), 7.65 (d, J = 8.1 Hz, 3 H), 7.60 (dd, 8.10, 1.4 Hz, 3H), 7.26 (d, J = 8.3 Hz, 6H), 6.87 (s, 3H), 2.80–3.00 (m, 12H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 154.7, 150.1, 142.7, 141.8, 137.4, 132.2, 131.4, 129.0 (2C), 126.7 (2C), 126.6, 119.9, 38.0, 37.9, 18.3. LRMS: 663. HRMS : calculated = 663.3613; found = 663.3613.

(GSTP-C1-164) **[Ir•HC2]**

To a suspention of **HC2** (50 mg, 0.075 mmol, 1.0 equiv.) in ethylene glycol (7.5 mL) was added $Ir(acac)_3$ (37 mg, 0.075 mmol, 1.0 equiv.). The mixture was degassed twice and heated at 250°C for 24 h. The reaction was followed by TLC. The reaction was poured into H_2O/DCM (1:1, 50 mL). The phases were separated and the aqueous phase was extract with DCM (5 x 25 mL). The organic phases were combined and dried over $MgSO_4$. The organic phase was filtered and then concentrated under reduced pressure. The crude was purified by flash chromatography (30% hexanes/DCM on silica) to yield 21 mg of a yellow solid (33%, dec. 265°C). The compound was crystallized by slow evaporation of a solution of Ir•HC2 in $CHCl_3$. Rf(30% hexanes/DCM): 0.30. ^{1}H NMR (600 MHz, CD_2Cl_2): δ 7.71 (d, J = 8.3 Hz, 3H), 7.54 (d, J = 7.8 Hz, 3H), 7.41 (dd, J = 8.3, 1.3 Hz, 3H), 7.35 (s, 3H), 6.59 (d, J = 7.7 Hz, 3H), 6.51 (s, 3H), 5.39 (br, 3H), 3.06 (dt, J = 12.9, 3.5 Hz, 3H), 2.72 (dt, J = 12.3, 3.6 Hz, 3H), 2.49 (td, J = 13.0, 3.6 Hz, 3H), 2.39 (dt, J = 13.3, 3.3 Hz, 3H), 2.15 (s, 9H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 164.3, 160.3, 147.5, 142.2, 140.6, 139.8, 137.3, 131.8, 127.9, 123.7, 120.8, 118.5, 38.5, 37.2, 18.5. LRMS : 853. HRMS : calculated = 853.3008; found = 853.3012.

X-Ray Crystallography. The crystals were grown by slow evaporation of a chloroform solution. One single crystal of 0.30 X 0.30 X 0.40 mm^3 for **Ir.HC2** was mounted using a glass fiber on the goniometer. Data were collected on an Enraf-Nonius CAD-4 automatic diffractometer at the Université de Sherbrooke using omega scans at 198(2) K. The DIFRAC[6] program was used for centering, indexing, and data collection. One standard reflection was measured every 100 reflections, no intensity decay was observed during data collection. The data were corrected for absorption by empirical methods based on psi scans and reduced with the NRCVAX[7] programs. They were solved using SHELXS-97[8] and refined by full-matrix least squares on F2 with SHELXL-97.[8] The non-hydrogen atoms were refined anisotropically. The hydrogen atoms were placed at idealized calculated geometric position and refined isotropically using a riding model. A summary of the refinement parameters and the resulting factors for **Ir.HC2** is given in Table S1.

Table S1. Crystallographic data for **Ir.HC2**.



Ir-HC-2	
Identification code	GSTP-C1-194
Empirical formula	C51 H45 Cl9 Ir N3
Formula weight	1211.15
Temperature	193(2) K
Wavelength	0.71073 Å
Crystal system	Hexagonal
Space group	R-3
Unit cell dimensions	a = 16.655(9) Å α= 90°.
	b = 16.655 Å β= 90°.
	c = 29.156(13) Å γ = 120°.
Volume	7004(5) Å^3
Z	6
Density (calculated)	1.723 Mg/m^3
Absorption coefficient	3.416 mm^{-1}
F(000)	3612
Crystal size	0.40 x 0.30 x 0.30 mm^3
Theta range for data collection	1.58 to 25.53°.
Index ranges	-16<=h<=17, 0<=k<=20, 0<=l<=35
Reflections collected	2911
Independent reflections	2911 [R(int) = 0.0000]
Completeness to theta = 25.50°	1
Absorption correction	Psi-Scan
Max. and min. transmission	0.4272 and 0.3419
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2911 / 0 / 195
Goodness-of-fit on F^2	0.991
Final R indices [I>2sigma(I)]	R1 = 0.0677, wR2 = 0.1628
R indices (all data)	R1 = 0.0890, wR2 = 0.1724
Extinction coefficient	0.00014(7)
Largest diff. peak and hole	3.369 and -4.531 e.Å^{-3}

Photophysical characterization. All samples were prepared in either 2-methyltetrahydrofuran (2-MeTHF), which was filtered over an alumina column then distilled over CaH_2 under nitrogen, butyronitrile (BuCN), which was treated with charcoal for 20 h, K_2CO_3 and alumina for 20h and finally distilled over P_2O_5 under nitrogen, HPLC grade acetonitrile (ACN) or spectroscopic grade methanol (MeOH) and ethanol (EtOH). Each sample was diluted to a concentration on the order of 25 μM.

Absorption spectra were recorded at room temperature and at 77 K in a 1.0 cm capped quartz cuvette and an NMR tube inserted into a liquid nitrogen filled quartz dewar, respectively, using a Shimadzu UV-1800 double beam spectrophotometer. Molar absorptivity determination was verified by linear least squares fit of values obtained from at least three independent solutions at varying concentrations with absorbances ranging from 0.01-2.6.

Steady-state emission spectra were obtained by exciting at the lowest energy absorption maxima using a Horiba Jobin Yvon Fluorolog-3 spectrofluorometer equipped with double monochromators and using the optically dilute method.[9 10] A stock solution with absorbance of ca. 0.5 was prepared and then four dilutions were prepared with dilution factors of 40, 20, 13.3 and 10 to obtain solutions with absorbances of ca. 0.013, 0.025, 0.038 and 0.05. The Beer-Lambert law was found to be linear at the concentrations of the solutions. Samples were placed into using septa sealed quartz cells and solutions were degassed with solvent-saturated nitrogen for 20 minutes prior to spectrum acquisition. For each sample, linearity between absorption and emission intensity was verified and additional measurement were undertaken until the Pearson regression factor (R^2) for the linear fit of the data set registered at least 0.9. Individual relative quantum yield values were calculated for each solution and the values reported represent the arithmetic mean of these results. The equation $\Phi_s = \Phi_r(A_r/A_s)(I_s/I_r)(n_s/n_r)^2$ was used to calculate the relative quantum yield of each of the sample, where Φ_r is the absolute quantum yield of the reference, n is the refractive index of the solvent, A is the absorbance at the excitation wavelength, and I is the integrated area under the corrected emission curve. The subscripts s and r refer to the sample and reference, respectively. A solution of $[Ru(bpy)_3](PF_6)_2$ in ACN (Φ_r = 9.5 %) or in water (Φ_r = 4.0 %) was used as the external reference.[11] Quantum yield measurements were found to be statistically reproducible, with the experimental uncertainty found to be on the order of (3 %). We have never the less conservatively estimated the error to be 10 %.

Time-resolved excited-state lifetime measurements were determined using the time-correlated single photon counting (TCSPC) option of the Jobin Yvon Fluorolog-3 spectrofluorometer. A pulsed NanoLED at 341 nm (pulse duration < 1 ns; fwhm = 14 nm), mounted directly on the sample chamber at 90° to the emission monochromator, was used to excite the samples and photons were collected using a FluoroHub from Horiba Jobin Yvon single-photon-counting detector. The luminescence lifetimes were obtained using the commercially available Horiba Jobin Yvon Decay Analysis Software version 6.4.1, software included within the spectrofluorimeter. Lifetimes were determined though an assessment of the goodness of its mono exponentially decaying fit by minimizing the chi squared function (χ^2) and by visual inspection of the weighted residuals.

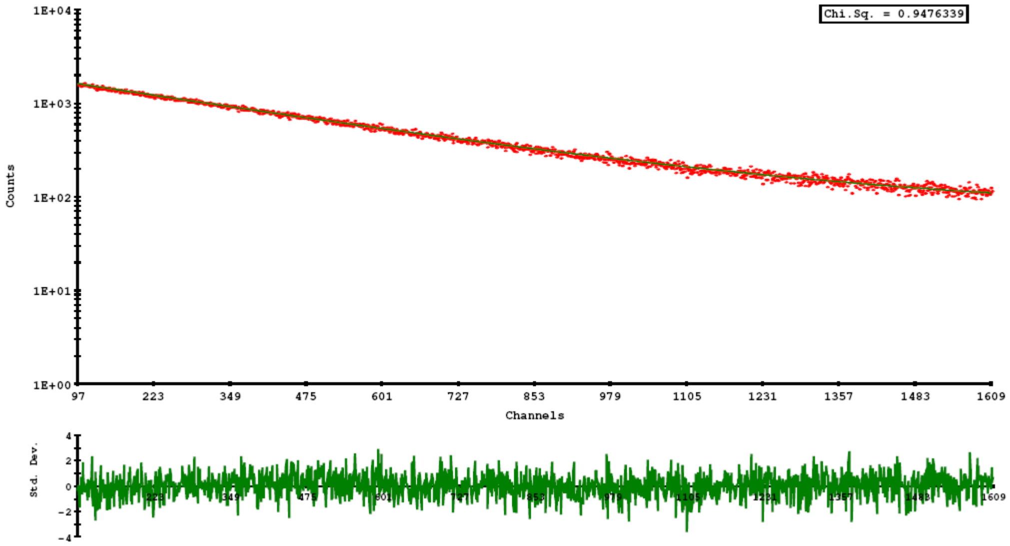


Figure S1: Example of a lifetime measurement of sample **Ir.HC1** in BuCN at 298K. Decay curves in red and standard deviation after modeling with a mono-exponential regression, in green.

Computational Methodology. Calculations were performed with Gaussian 09[12] at the Université de Sherbrooke with Mammouth super computer supported by le Réseau Québécois de Calculs de Haute Performances. The DFT[13] and TD-DFT[14] were calculated with the B3LYP[15] method. 3-21G*[16] basis sets were used for C, H and N, VDZ (valence double ζ) with SBKJC effective core potentials[16a,17] for Iridium. The predicted phosphorescence wavelengths were obtained by energy differences between the Triplet and Singlet optimized states.[5] The calculated absorption spectra and related MO contributions were obtained from the TD-DFT/Singlets output file and gausssum 2.1.[18]

Absorption and Emission spectroscopy.

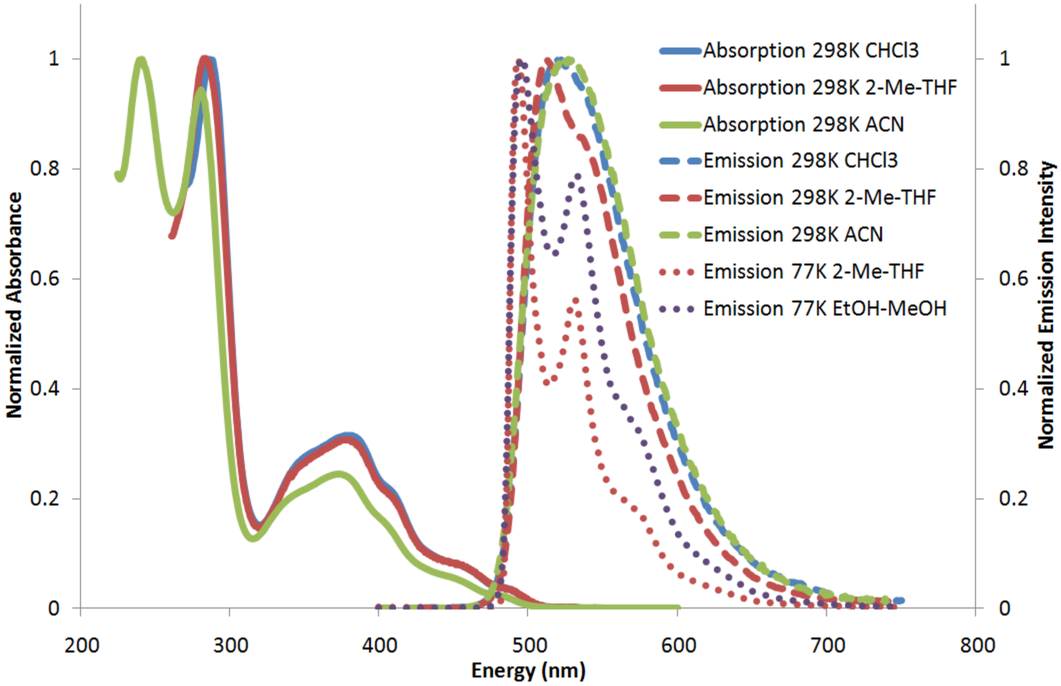


Figure S2. Absorption (solid line) and emission spectra at 298 K (dashed line) and at 77 K (dotted line) of *fac*-Ir(ppy)$_3$ in chloroform (CHCl$_3$, **blue**), 2-methyl-tetrahydrofurane (2-MeTHF, **red**), acetonitrile (ACN, **green**) and ethanol/methanol (1/1) mixture (EtOH-MeOH, **purple**).

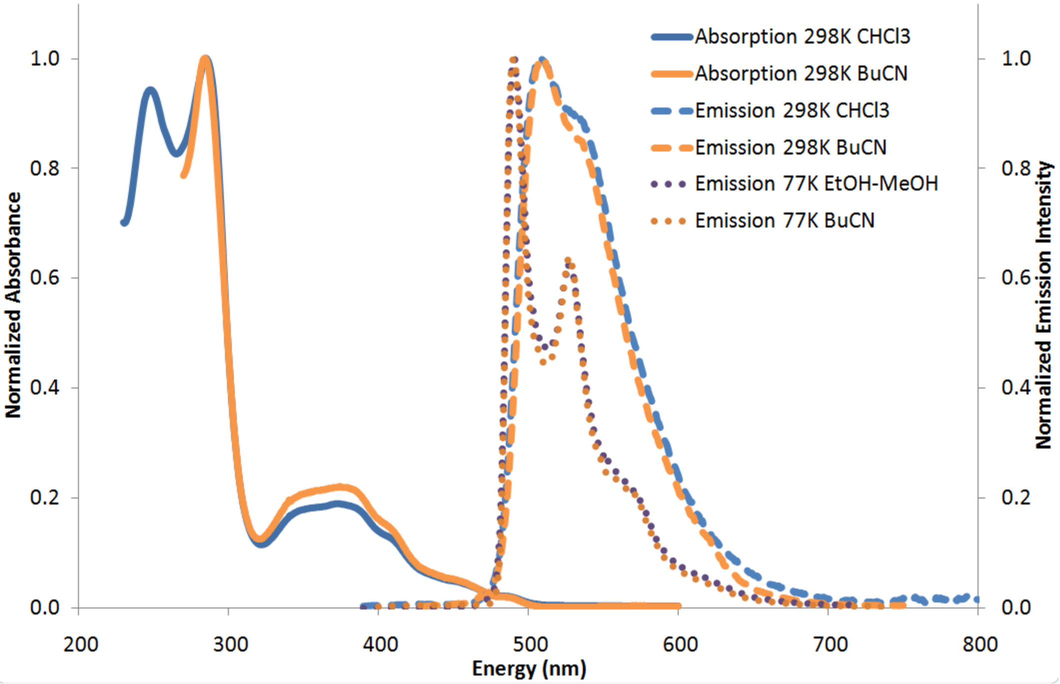


Figure S3. Absorption (solid line) and emission spectra at 298 K (dashed line) and at 77 K (dotted line) of **[Ir.HC1]** in chloroform (CHCl$_3$, **blue**), butyronitrile (BuCN, **orange**) and ethanol/methanol (1/1) mixture (EtOH-MeOH, **purple**).

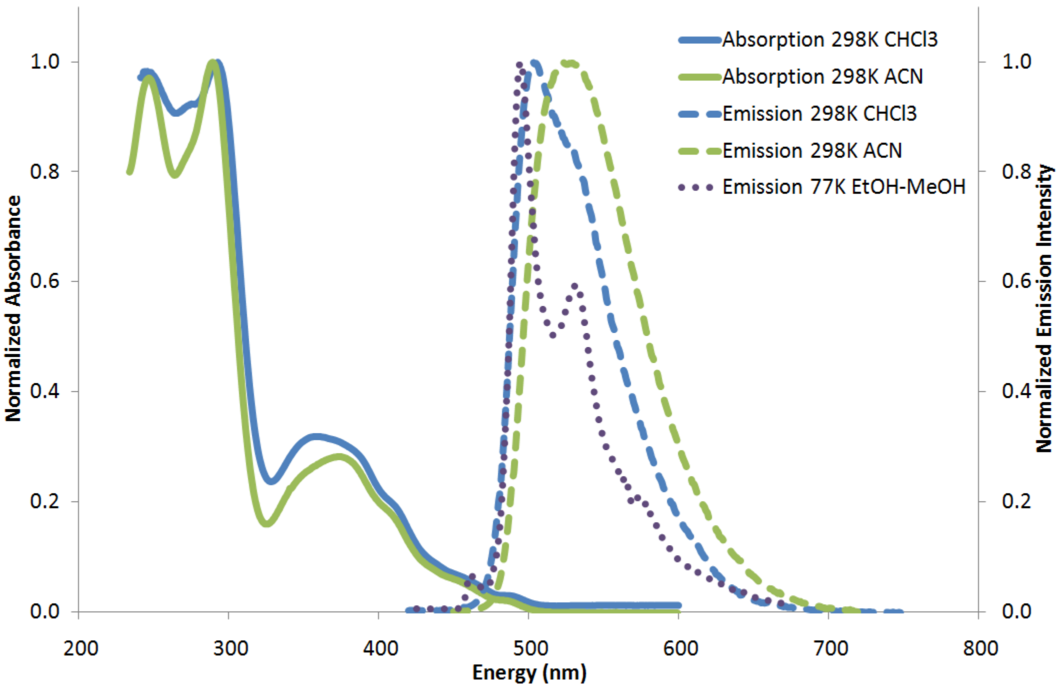


Figure S4. Absorption (solid line) and emission spectra at 298 K (dashed line) and at 77 K (dotted line) of **[Ir.HC2]** in chloroform ($CHCl_3$, **blue**), acetonitrile (ACN, **green**) and ethanol/methanol (1/1) mixture (EtOH-MeOH, **purple**).

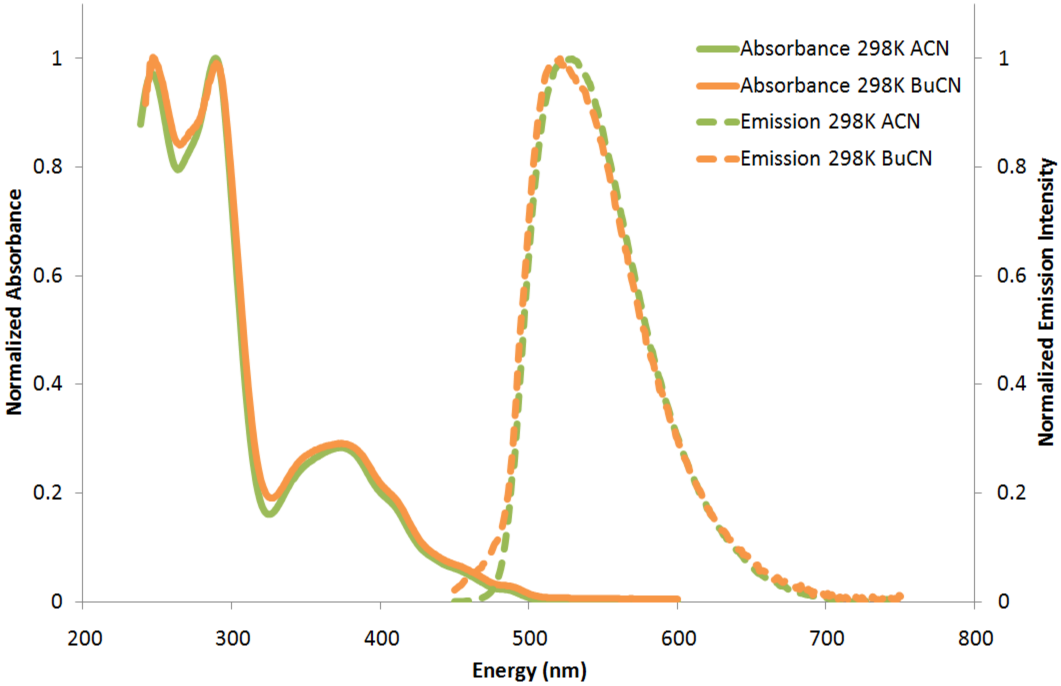


Figure S5 Absorption (solid line) and emission spectra at 298 K (dashed line) of **[Ir.HC2]** in acetonitrile (ACN, **green**) and butyronitrile (BuCN, **orange**).

TD-DFT simulated absorption spectra.

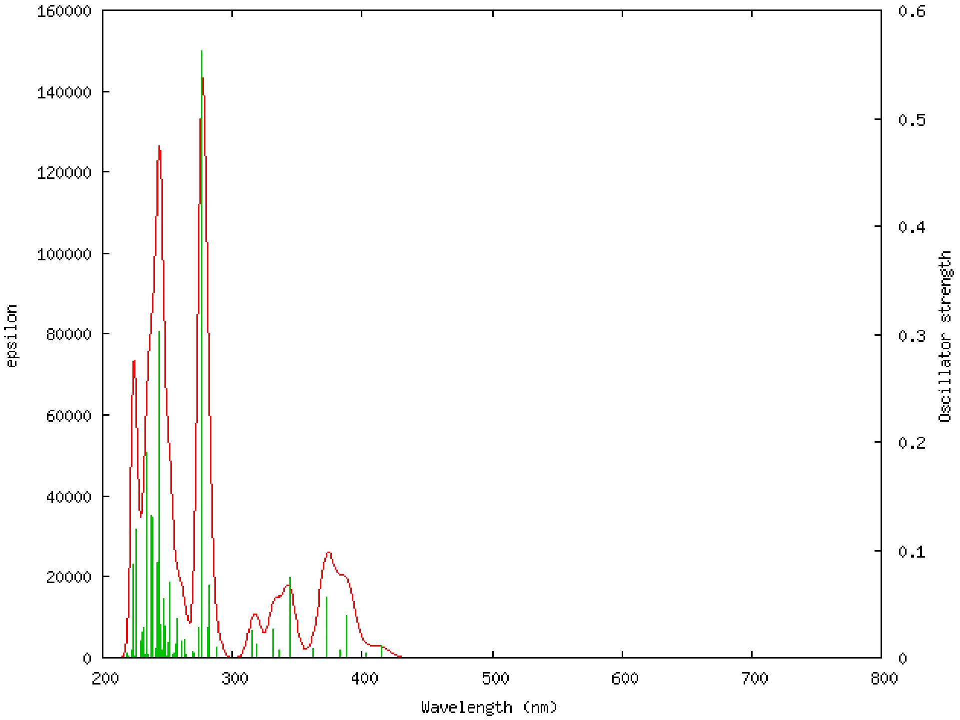


Figure S6. TD-DFT simulated absorption spectra for **[Ir.HC1]**

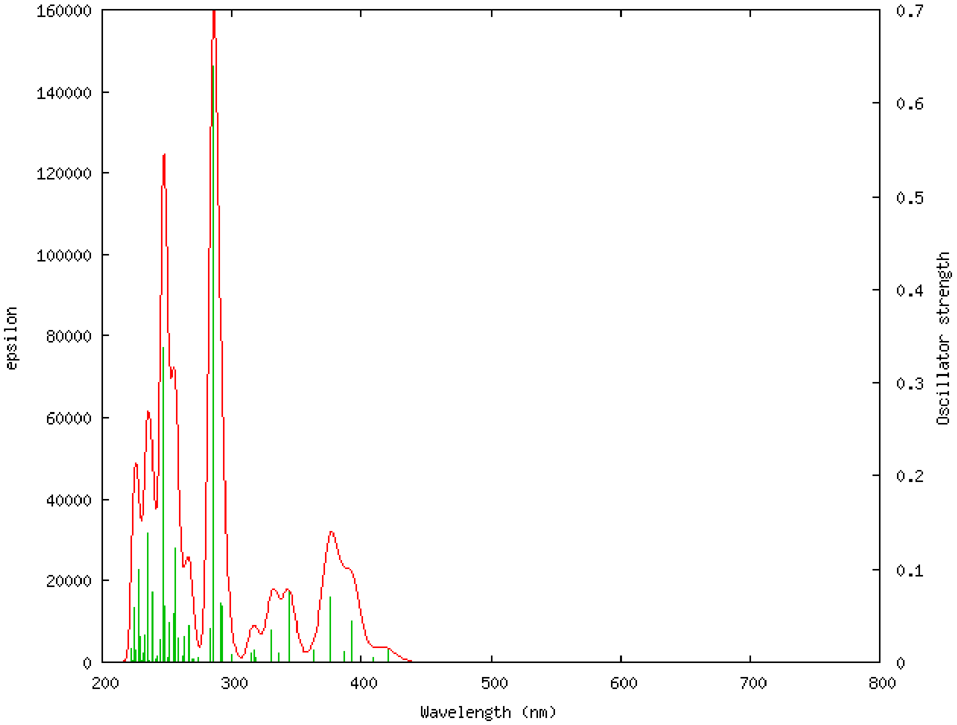


Figure S7. TD-DFT simulated absorption spectra for **[Ir.HC2]**

Visualisation of selected MOs.

Table S2. Visualisation of selected MOs for **[Ir.HC1]**

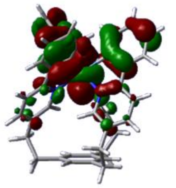
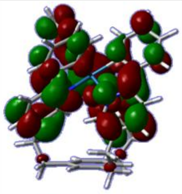
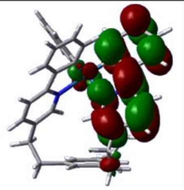
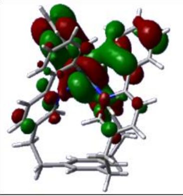
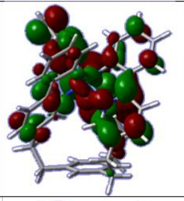
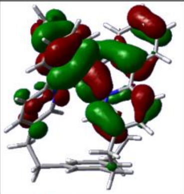
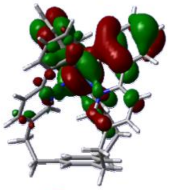
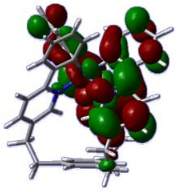
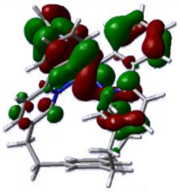
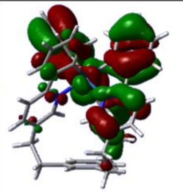
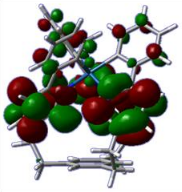
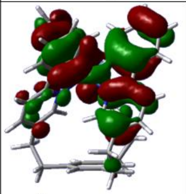
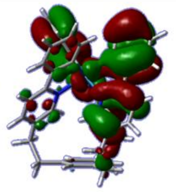
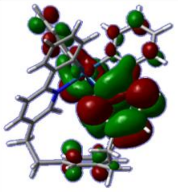
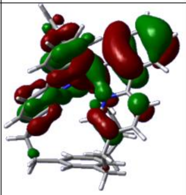
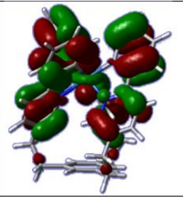
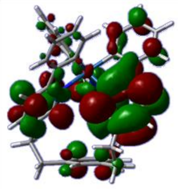
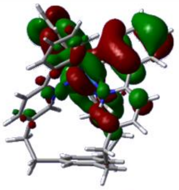
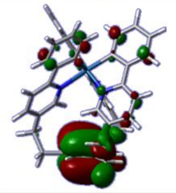
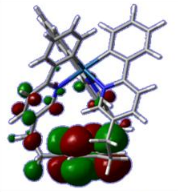
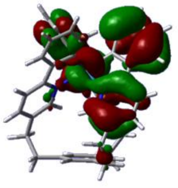
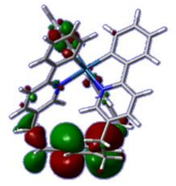
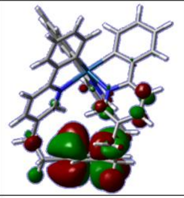
Orbital Energy (eV)	Image	Orbital Energy (eV)	Image	Orbital Energy (eV)	Image
S0 HOMO -5.14		S0 LUMO -1.39		T1 HSOMO -2.78	
S0 HOMO-1 -5.31		S0 LUMO+1 -1.25		T1 HSOMO-1 -5.47	
S0 HOMO-2 -5.31		S0 LUMO+2 -1.25		T1 HSOMO-2 -5.71	
S0 HOMO-3 -6.20		S0 LUMO+3 -0.93		T1 HSOMO-3 -5.71	
S0 HOMO-4 -6.20		S0 LUMO+4 -0.73		T1 HSOMO-4 -5.74	
S0 HOMO-5 -6.34		S0 LUMO+5 -0.73		T1 HSOMO-5 -5.77	
S0 HOMO-6 -6.67		S0 LUMO+6 -0.08		T1 HSOMO-6 -5.80	
S0 HOMO-7 -6.75		S0 LUMO+7 -0.08			

Table S3. Visualisation of selected MOs for **[Ir.HC2]**

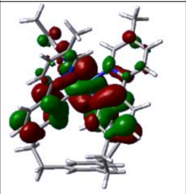
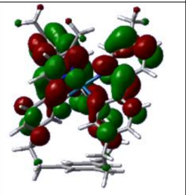
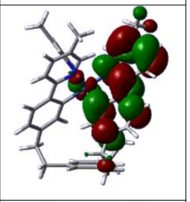
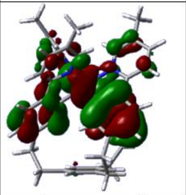
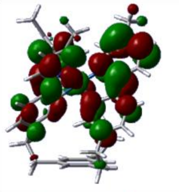
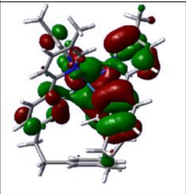
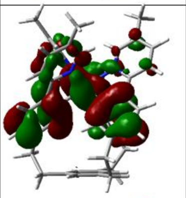
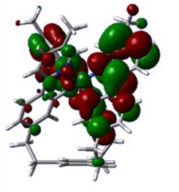
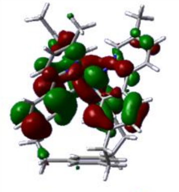
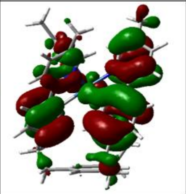
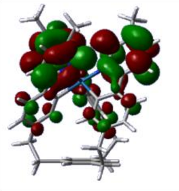
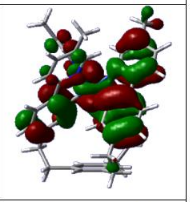
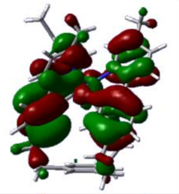
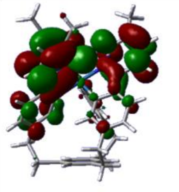
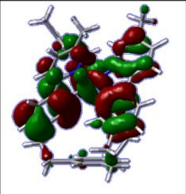
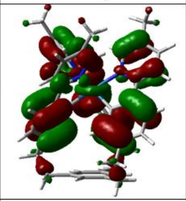
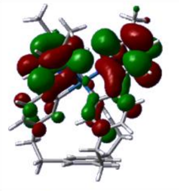
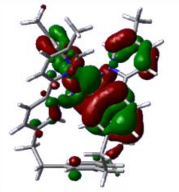
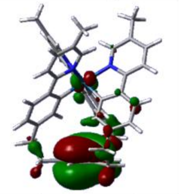
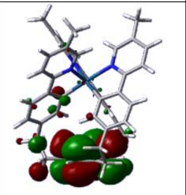
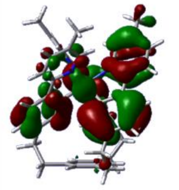
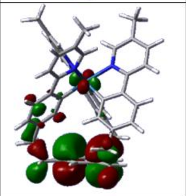
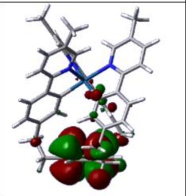
Orbital Energy (eV)	Image	Orbital Energy (eV)	Image	Orbital Energy (eV)	Image
S0 HOMO -5.06		S0 LUMO -1.33		T1 HSOMO -2.72	
S0 HOMO-1 -5.20		S0 LUMO+1 -1.22		T1 HSOMO-1 -5.36	
S0 HOMO-2 -5.20		S0 LUMO+2 -1.22		T1 HSOMO-2 -5.52	
S0 HOMO-3 -5.99		S0 LUMO+3 -0.84		T1 HSOMO-3 -5.61	
S0 HOMO-4 -5.99		S0 LUMO+4 -0.63		T1 HSOMO-4 -5.63	
S0 HOMO-5 -6.15		S0 LUMO+5 -0.63		T1 HSOMO-5 -5.66	
S0 HOMO-6 -6.39		S0 LUMO+6 0.11		T1 HSOMO-6 -5.69	
S0 HOMO-7 -6.39		S0 LUMO+7 0.11			

Table S4. Energy and composition of TD-DFT calculated transitions for **[Ir.HC1]**

No.	Energy (cm^{-1})	Wavelength (nm)	Oscillator Strength	Symmetry	Major contributions
1	24125.02	414.507494	0.0106	Singlet-A	HOMO->LUMO (97%)
2	24775.1	403.631008	0.0039	Singlet-A	HOMO->L+1 (96%)
3	24782.36	403.51278	0.0039	Singlet-A	HOMO->L+2 (96%)
4	25778.46	387.920705	0.0394	Singlet-A	H-1->LUMO (90%)
5	25787.34	387.787241	0.0386	Singlet-A	H-2->LUMO (90%)
6	26122.87	382.806399	0.0075	Singlet-A	H-2->L+1 (33%), H-2->L+2 (-14%), H-1->L+1 (15%), H-1->L+2 (34%)
7	26799.57	373.140328	0.0554	Singlet-A	H-2->L+1 (46%), H-1->L+2 (-46%)
8	26802.8	373.095413	0.0562	Singlet-A	H-2->L+2 (45%), H-1->L+1 (46%)
9	27625.49	361.984575	0.0079	Singlet-A	H-2->L+2 (-24%), H-1->L+1 (23%), HOMO->L+3 (33%)
10	29073.26	343.958655	0.0742	Singlet-A	H-2->L+2 (10%), H-1->L+1 (-10%), HOMO->L+3 (64%)
11	29705.6	336.636809	0.0069	Singlet-A	H-1->L+3 (93%)
12	29719.32	336.481495	0.0071	Singlet-A	H-2->L+3 (93%)
13	30119.37	332.012256	0.0258	Singlet-A	HOMO->L+4 (92%)
14	30135.5	331.834533	0.0259	Singlet-A	HOMO->L+5 (92%)
15	31334.86	319.133428	0.0029	Singlet-A	H-2->L+4 (-29%), H-2->L+5 (-11%), H-1->L+4 (32%), H-1->L+5 (-26%)
16	31396.15	318.510344	0.0123	Singlet-A	H-2->L+4 (-48%), H-1->L+5 (49%)
17	31397.77	318.49398	0.0123	Singlet-A	H-2->L+5 (56%), H-1->L+4 (39%)
18	31684.1	315.615754	0.0255	Singlet-A	H-2->L+4 (-19%), H-2->L+5 (29%), H-1->L+4 (-23%), H-1->L+5 (-20%)
19	34644.17	288.648841	0.0099	Singlet-A	H-3->LUMO (93%)
20	34657.08	288.541359	0.0103	Singlet-A	H-4->LUMO (93%)
21	35454.76	282.04954	0.0022	Singlet-A	H-4->L+1 (28%), H-3->L+1 (-26%), H-3->L+2 (34%)
22	35483.8	281.81874	0.0646	Singlet-A	H-4->L+2 (49%), H-3->L+1 (40%)
23	35488.64	281.780311	0.0667	Singlet-A	H-4->L+1 (49%), H-3->L+2 (-42%)
24	35576.56	281.083989	0.0273	Singlet-A	H-5->LUMO (34%), H-4->L+2 (30%), H-3->L+1 (-21%)
25	36142.76	276.680584	0.5618	Singlet-A	H-5->LUMO (54%)
26	36427.48	274.51806	0.0273	Singlet-A	H-5->L+1 (87%)
27	36434.73	274.463367	0.027	Singlet-A	H-5->L+2 (87%)
28	37030.78	270.045602	0.0038	Singlet-A	HOMO->L+6 (98%)
29	37038.85	269.986796	0.0037	Singlet-A	HOMO->L+7 (98%)
30	37200.97	268.810218	0.0058	Singlet-A	H-8->LUMO (86%)
31	37859.12	264.13715	0.0025	Singlet-A	H-8->L+1 (79%)
32	37867.19	264.080889	0.002	Singlet-A	H-8->L+2 (78%)
33	37970.43	263.362866	0.0159	Singlet-A	H-6->LUMO (38%), H-4->L+3 (17%), H-3->L+3 (-18%)
34	37976.07	263.323712	0.0166	Singlet-A	H-7->LUMO (37%), H-4->L+3 (18%), H-3->L+3 (18%)
35	38212.39	261.695204	0.0003	Singlet-A	H-2->L+6 (30%), H-1->L+6 (-19%), H-1->L+7 (46%)
36	38231.75	261.562703	0.0004	Singlet-A	H-2->L+7 (13%), H-1->L+6 (66%), H-1->L+7 (15%)
37	38236.59	261.529598	0.0002	Singlet-A	H-2->L+6 (58%), H-1->L+7 (-32%)
38	38258.37	261.380732	0.0015	Singlet-A	H-2->L+7 (77%)
39	38380.96	260.545826	0.0152	Singlet-A	H-7->LUMO (-11%), H-6->LUMO (36%), H-4->L+3 (-16%), H-3->L+3 (20%)

40	38385	260.518452	0.0153	Singlet-A	H-7->LUMO (37%), H-6->LUMO (10%), H-4->L+3 (-21%), H-3->L+3 (-15%)
41	38823.77	257.574191	0.0367	Singlet-A	H-7->L+1 (-17%), H-7->L+2 (-12%), H-6->L+1 (-13%), H-6->L+2 (17%), H-5->L+3 (-16%)
42	38969.75	256.609274	0.0126	Singlet-A	H-11->LUMO (28%), HOMO->L+8 (40%)
43	39107.67	255.704285	0.0047	Singlet-A	H-9->LUMO (22%), H-7->L+1 (24%), H-6->L+2 (25%)
44	39111.71	255.677919	0.0047	Singlet-A	H-10->LUMO (20%), H-7->L+2 (-24%), H-6->L+1 (29%)
45	39244.79	254.810894	0.001	Singlet-A	H-7->L+2 (27%), H-6->L+1 (30%), HOMO->L+8 (-20%)
46	39267.37	254.664346	0.0017	Singlet-A	H-9->LUMO (30%), H-7->L+1 (-20%), H-6->L+2 (-17%)
47	39274.63	254.617277	0.002	Singlet-A	H-10->LUMO (31%), H-7->L+2 (22%), H-6->L+1 (-12%)
48	39453.69	253.461723	0.0024	Singlet-A	H-7->L+1 (-14%), H-6->L+2 (13%), H-5->L+3 (47%)
49	39648.07	252.219087	0.0705	Singlet-A	H-11->LUMO (21%), H-4->L+4 (-11%), HOMO->L+8 (-16%)
50	39677.91	252.029387	0.0064	Singlet-A	H-3->L+4 (-12%), HOMO->L+9 (33%)
51	39683.56	251.99353	0.0056	Singlet-A	H-3->L+5 (12%), HOMO->L+10 (32%)
52	39777.12	251.400808	0.0674	Singlet-A	H-11->LUMO (15%), H-4->L+4 (14%), H-3->L+5 (13%)
53	39883.59	250.729715	0.0136	Singlet-A	H-4->L+5 (-11%), H-3->L+4 (-14%), H-2->L+8 (-10%), H-1->L+8 (21%), HOMO->L+10 (13%)
54	39884.39	250.724644	0.0145	Singlet-A	H-4->L+4 (13%), H-3->L+5 (-12%), H-2->L+8 (20%), H-1->L+8 (10%), HOMO->L+9 (13%)
55	40036.83	249.770013	0.0011	Singlet-A	H-5->L+3 (-10%), H-4->L+5 (43%), H-3->L+4 (-39%)
56	40289.29	248.20495	0.0274	Singlet-A	H-11->L+2 (-11%), H-10->L+2 (-12%), H-9->L+1 (13%)
57	40293.32	248.180108	0.0288	Singlet-A	H-11->L+1 (-11%), H-10->L+1 (13%), H-9->L+2 (12%)
58	40579.65	246.428957	0.0527	Singlet-A	H-9->L+1 (-15%), H-2->L+8 (40%)
59	40582.87	246.409366	0.0552	Singlet-A	H-1->L+8 (40%)
60	40605.46	246.27232	0.0067	Singlet-A	H-11->LUMO (16%), H-10->L+2 (38%), H-9->L+1 (19%)
61	40846.62	244.81831	0.0314	Singlet-A	H-11->L+1 (34%)
62	40854.68	244.769977	0.0302	Singlet-A	H-11->L+2 (34%)
63	41009.54	243.845681	0.3017	Singlet-A	H-10->L+1 (18%), H-9->L+2 (-17%), H-3->L+5 (-10%)
64	41042.61	243.649209	0.0106	Singlet-A	H-5->L+4 (78%)
65	41058.74	243.553484	0.0105	Singlet-A	H-5->L+5 (78%)
66	41312	242.0604	0.0233	Singlet-A	H-8->L+3 (48%), H-2->L+10 (-13%), H-1->L+9 (14%)
67	41326.52	241.975363	0.0881	Singlet-A	H-8->L+3 (30%), H-2->L+10 (12%), H-1->L+9 (-13%)
68	41455.57	241.222103	0.0049	Singlet-A	H-12->LUMO (54%), H-6->L+3 (-15%)
69	41460.41	241.193947	0.0051	Singlet-A	H-13->LUMO (55%), H-7->L+3 (11%)
70	41498.32	240.973619	0.0083	Singlet-A	H-6->L+3 (75%)

71	41508	240.917429	0.0087	Singlet-A	H-7->L+3 (80%)
72	41985.48	238.177575	0.1297	Singlet-A	H-2->L+10 (19%), H-1->L+9 (19%)
73	41995.16	238.122682	0.132	Singlet-A	H-2->L+9 (20%), H-1->L+10 (-19%)
74	42052.43	237.798413	0.0064	Singlet-A	H-13->L+1 (19%), H-13->L+2 (23%), H-12->L+1 (-23%), H-12->L+2 (18%)
75	42117.76	237.42955	0.0001	Singlet-A	H-7->L+4 (31%), H-7->L+6 (-15%), H-6->L+5 (-31%), H-6->L+7 (15%)
76	42596.05	234.76357	0.0029	Singlet-A	H-13->L+1 (34%), H-12->LUMO (16%), H-12->L+2 (-32%)
77	42596.85	234.759125	0.003	Singlet-A	H-13->LUMO (16%), H-13->L+2 (33%), H-12->L+1 (33%)
78	42687.99	234.257901	0.1899	Singlet-A	H-2->L+9 (11%), H-1->L+10 (11%), HOMO->L+11 (39%)
79	42772.68	233.794076	0	Singlet-A	H-13->L+1 (25%), H-13->L+2 (-19%), H-12->L+1 (18%), H-12->L+2 (26%)
80	42934.8	232.911288	0.0031	Singlet-A	H-8->L+4 (76%)
81	42951.74	232.81944	0.003	Singlet-A	H-8->L+5 (77%)
82	43217.1	231.389901	0.0071	Singlet-A	H-9->L+3 (-22%), H-6->L+4 (49%)
83	43222.74	231.359676	0.0049	Singlet-A	H-10->L+3 (19%), H-9->L+3 (-12%), H-7->L+4 (22%), H-6->L+4 (-14%), H-6->L+5 (22%)
84	43242.1	231.256107	0.0282	Singlet-A	H-7->L+5 (70%), H-6->L+4 (14%)
85	43446.97	230.165661	0.0235	Singlet-A	H-9->L+3 (46%), H-7->L+4 (14%), H-6->L+5 (14%)
86	43455.84	230.118669	0.0239	Singlet-A	H-10->L+3 (48%), H-7->L+5 (-15%), H-6->L+4 (12%)
87	43649.41	229.09815	0.0147	Singlet-A	H-11->L+3 (78%)
88	44235.78	226.06133	0.1187	Singlet-A	HOMO->L+11 (32%)
89	44254.33	225.966568	0.01	Singlet-A	HOMO->L+14 (51%)
90	44273.69	225.867771	0.0118	Singlet-A	H-2->L+14 (-10%), HOMO->L+15 (48%)
91	44539.86	224.518012	0.0007	Singlet-A	H-7->L+4 (-13%), H-7->L+6 (-19%), H-6->L+5 (13%), H-6->L+7 (19%)
92	44710.04	223.663407	0.0863	Singlet-A	H-1->L+11 (70%)
93	44718.11	223.623066	0.0851	Singlet-A	H-2->L+11 (72%)
94	44831.02	223.059814	0.0339	Singlet-A	H-11->L+4 (15%), H-10->L+4 (-18%), H-9->L+5 (-18%), HOMO->L+12 (22%)
95	44834.25	223.043763	0.0311	Singlet-A	H-11->L+5 (15%), H-10->L+5 (17%), H-9->L+4 (-19%), HOMO->L+12 (10%), HOMO->L+13 (20%)
96	44882.64	222.803272	0.0063	Singlet-A	H-10->L+4 (23%), H-9->L+5 (-20%), H-2->L+14 (-16%), H-1->L+15 (16%)
97	44966.53	222.387646	0.0071	Singlet-A	HOMO->L+12 (53%)
98	44975.4	222.343776	0.0076	Singlet-A	HOMO->L+13 (55%)
99	45386.74	220.328648	0.0007	Singlet-A	H-10->L+5 (40%), H-9->L+4 (39%)
100	45590.8	219.34248	0.0045	Singlet-A	H-4->L+6 (37%), H-3->L+7 (42%)

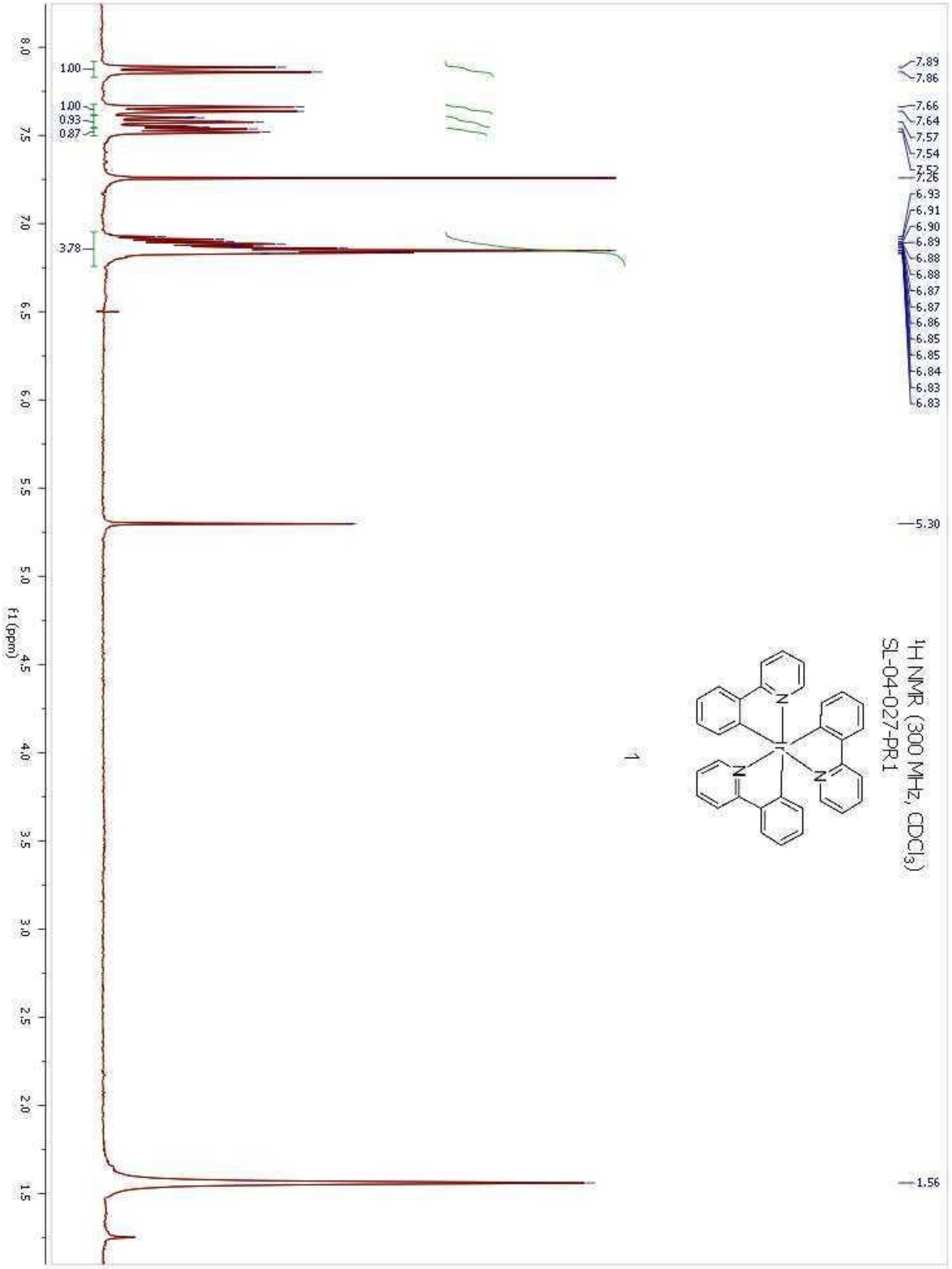
Table S5. Energy and composition of TD-DFT calculated transitions for **[Ir.HC2]**

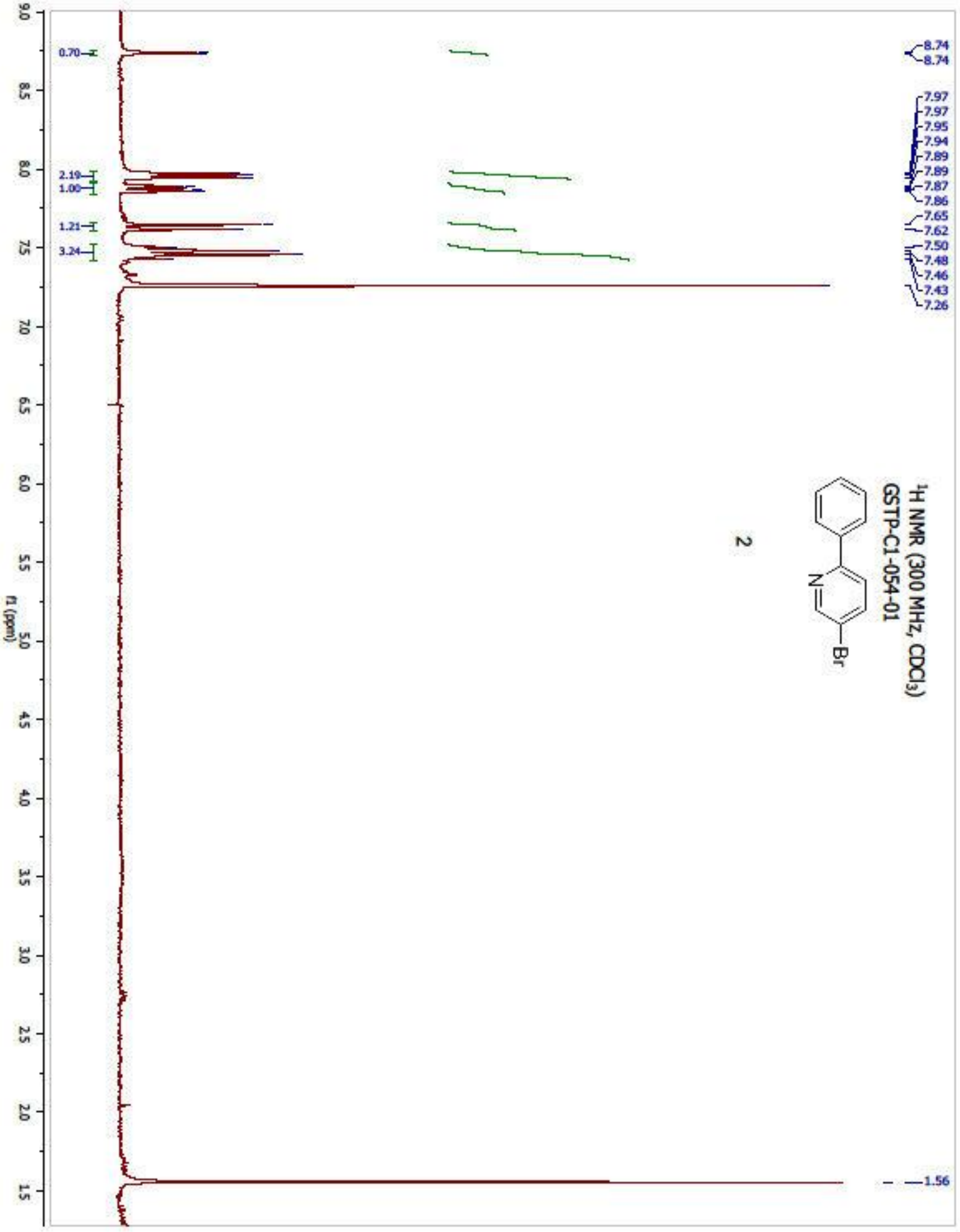
No.	Energy (cm^{-1})	Wavelength (nm)	Oscillator Strength	Symmetry	Major contributions
1	23784.65	420.439271	0.0131	Singlet-A	HOMO->LUMO (98%)
2	24457.32	408.875562	0.0047	Singlet-A	HOMO->L+1 (95%)
3	24461.35	408.808153	0.0046	Singlet-A	HOMO->L+2 (95%)
4	25496.97	392.203393	0.0436	Singlet-A	H-2->LUMO (-21%), H-1->LUMO (69%)
5	25501.81	392.128967	0.0437	Singlet-A	H-2->LUMO (69%), H-1->LUMO (21%)
6	25838.96	387.012538	0.012	Singlet-A	H-2->L+2 (48%), H-1->L+1 (49%)
7	26572.12	376.334305	0.0697	Singlet-A	H-2->L+1 (41%), H-1->L+2 (41%)
8	26576.15	376.277198	0.0707	Singlet-A	H-2->L+2 (42%), H-1->L+1 (-41%)
9	27502.08	363.608824	0.0138	Singlet-A	H-2->L+1 (35%), H-1->L+2 (-35%), HOMO->L+3 (26%)
10	29038.58	344.36946	0.0757	Singlet-A	H-2->L+1 (-12%), H-1->L+2 (12%), HOMO->L+3 (71%)
11	29773.36	335.870772	0.0097	Singlet-A	H-1->L+3 (93%)
12	29779.81	335.797998	0.0098	Singlet-A	H-2->L+3 (93%)
13	30224.22	330.860451	0.0339	Singlet-A	HOMO->L+4 (91%)
14	30227.45	330.825137	0.0341	Singlet-A	HOMO->L+5 (91%)
15	31438.1	318.085424	0.005	Singlet-A	H-2->L+4 (-46%), H-1->L+5 (52%)
16	31501.01	317.450166	0.0133	Singlet-A	H-2->L+4 (14%), H-2->L+5 (-33%), H-1->L+4 (36%), H-1->L+5 (12%)
17	31501.81	317.442038	0.0134	Singlet-A	H-2->L+4 (37%), H-2->L+5 (13%), H-1->L+4 (-14%), H-1->L+5 (33%)
18	31688.13	315.575587	0.0105	Singlet-A	H-2->L+5 (48%), H-1->L+4 (43%)
19	33327.87	300.049216	0.0073	Singlet-A	H-4->LUMO (16%), H-3->LUMO (77%)
20	33331.09	300.020173	0.0076	Singlet-A	H-4->LUMO (77%), H-3->LUMO (-16%)
21	34182.01	292.551526	0.0431	Singlet-A	H-4->L+1 (-15%), H-3->L+1 (60%)
22	34183.63	292.53772	0.0597	Singlet-A	H-4->L+1 (63%), H-4->L+2 (-13%), H-3->L+2 (16%)
23	34188.47	292.496312	0.034	Singlet-A	H-4->L+2 (38%), H-3->L+2 (53%)
24	34344.94	291.163723	0.0637	Singlet-A	H-5->LUMO (25%), H-4->L+1 (-16%), H-4->L+2 (-21%), H-3->L+1 (-19%), H-3->L+2 (16%)
25	34961.96	286.025184	0.6404	Singlet-A	H-5->LUMO (62%), H-4->L+2 (11%), H-3->L+1 (11%)
26	35326.52	283.073441	0.0349	Singlet-A	H-5->L+1 (88%)
27	35331.36	283.034669	0.0354	Singlet-A	H-5->L+2 (88%)
28	36460.54	274.269078	0.0041	Singlet-A	H-8->LUMO (91%)
29	36897.7	271.0196	0.003	Singlet-A	H-6->LUMO (68%), H-3->L+3 (-13%)
30	36905.77	270.96037	0.0031	Singlet-A	H-7->LUMO (68%), H-4->L+3 (-13%)
31	37125.15	269.359179	0.0025	Singlet-A	H-8->L+1 (73%)
32	37130.8	269.318222	0.0023	Singlet-A	H-8->L+2 (73%)
33	37426	267.19395	0.0396	Singlet-A	H-6->LUMO (23%), H-3->L+3 (54%)
34	37431.64	267.153648	0.0393	Singlet-A	H-7->LUMO (23%), H-4->L+3 (53%)
35	37516.33	266.55058	0.0063	Singlet-A	HOMO->L+6 (87%)
36	37524.4	266.493287	0.0058	Singlet-A	HOMO->L+7 (87%)
37	37943	263.55321	0.0272	Singlet-A	H-7->L+1 (12%), H-7->L+2 (20%), H-6->L+1 (23%), H-6->L+2 (-12%)
38	38059.15	262.748928	0.0015	Singlet-A	H-7->L+1 (-27%), H-7->L+2 (12%), H-6->L+1 (17%), H-6->L+2 (33%)

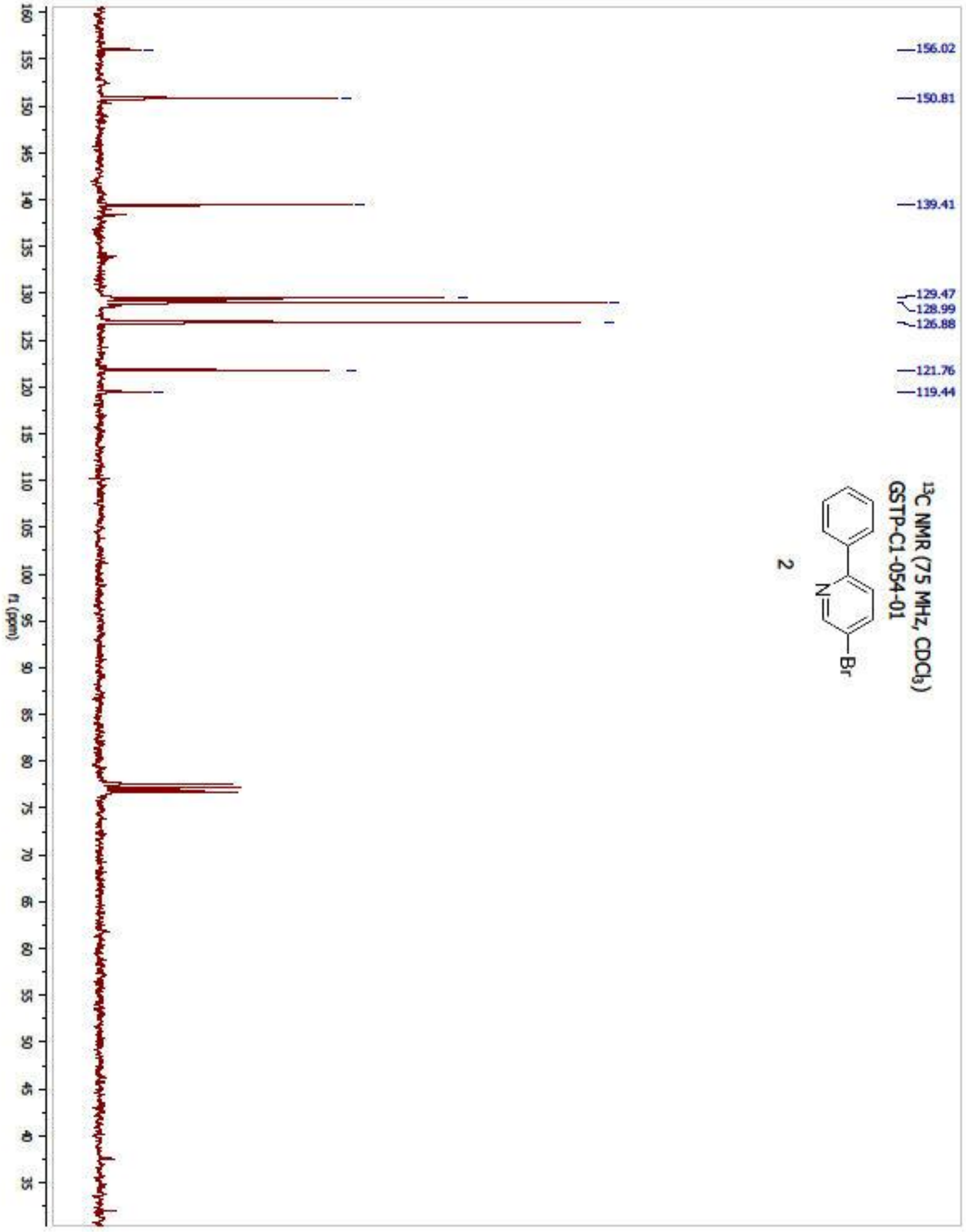
39	38111.57	262.38749	0.0058	Singlet-A	H-7->L+1 (43%), H-6->L+2 (37%)
40	38113.19	262.376384	0.0058	Singlet-A	H-7->L+2 (44%), H-6->L+1 (-36%)
41	38581.8	259.189582	0.0258	Singlet-A	H-5->L+3 (65%)
42	38630.19	258.864885	0.0012	Singlet-A	H-2->L+6 (-22%), H-2->L+7 (18%), H-1->L+6 (30%), H-1->L+7 (19%)
43	38662.45	258.648872	0.0012	Singlet-A	H-9->LUMO (30%), H-2->L+6 (15%), H-2->L+7 (-10%), H-1->L+6 (10%), H-1->L+7 (10%)
44	38667.29	258.616501	0.0011	Singlet-A	H-10->LUMO (28%), H-2->L+7 (15%), H-1->L+6 (-10%), H-1->L+7 (15%)
45	38728.59	258.20717	0.0103	Singlet-A	H-2->L+6 (21%), H-1->L+6 (38%), H-1->L+7 (-11%), HOMO->L+8 (11%)
46	38737.46	258.148032	0.0007	Singlet-A	H-10->LUMO (-16%), H-2->L+6 (17%), H-1->L+7 (32%)
47	38738.27	258.142657	0.0034	Singlet-A	H-2->L+7 (47%)
48	38939.91	256.805934	0.122	Singlet-A	H-4->L+4 (-22%), H-3->L+5 (22%)
49	39160.1	255.361956	0.0518	Singlet-A	H-4->L+5 (13%), H-3->L+5 (-14%), HOMO->L+8 (27%)
50	39162.52	255.346178	0.0396	Singlet-A	H-9->LUMO (15%), H-4->L+5 (-16%), H-3->L+4 (26%)
51	39165.75	255.325144	0.0405	Singlet-A	H-10->LUMO (13%), H-4->L+4 (35%), H-3->L+5 (14%)
52	39260.11	254.711432	0.0268	Singlet-A	H-5->L+3 (-13%), H-4->L+4 (10%), H-4->L+5 (22%), H-3->L+4 (20%), H-3->L+5 (-10%)
53	39709.37	251.829742	0.0417	Singlet-A	H-11->LUMO (-12%), H-10->L+2 (-15%), H-9->L+1 (17%), HOMO->L+8 (-17%)
54	39798.9	251.263247	0.0325	Singlet-A	H-10->L+1 (11%), H-9->L+2 (-11%), HOMO->L+9 (30%)
55	39802.93	251.237789	0.0327	Singlet-A	H-10->L+2 (-12%), H-9->L+1 (-10%), HOMO->L+10 (28%)
56	39952.14	250.299464	0.0045	Singlet-A	H-10->L+1 (-11%), H-9->L+2 (12%), H-2->L+8 (-10%), HOMO->L+9 (34%)
57	39953.76	250.289359	0.0043	Singlet-A	H-10->L+2 (12%), H-9->L+1 (11%), H-1->L+8 (11%), HOMO->L+10 (35%)
58	40306.22	248.100648	0.0114	Singlet-A	H-11->LUMO (38%), H-10->L+1 (-17%), H-9->L+2 (-27%)
59	40315.1	248.046048	0.0597	Singlet-A	H-10->L+1 (10%), H-5->L+4 (41%), H-2->L+8 (-17%), H-1->L+8 (13%)
60	40315.9	248.041086	0.0602	Singlet-A	H-5->L+5 (42%), H-2->L+8 (12%), H-1->L+8 (19%)
61	40446.56	247.239788	0.3376	Singlet-A	H-11->LUMO (-13%), H-10->L+2 (15%), H-9->L+1 (-14%)
62	40549.8	246.610317	0.0205	Singlet-A	H-5->L+4 (33%), H-2->L+8 (12%), H-1->L+8 (-19%)
63	40553.03	246.590697	0.0205	Singlet-A	H-5->L+5 (33%), H-2->L+8 (-19%), H-1->L+8 (-11%)
64	40859.52	244.740987	0.0234	Singlet-A	H-12->LUMO (29%), H-11->L+1 (-26%)
65	40867.59	244.692685	0.0243	Singlet-A	H-13->LUMO (27%), H-11->L+2 (27%)
66	40885.33	244.586488	0.0002	Singlet-A	H-8->L+3 (86%)
67	41367.66	241.734751	0.007	Singlet-A	H-2->L+10 (36%), H-1->L+9 (42%)
68	41400.72	241.541665	0.0013	Singlet-A	H-12->LUMO (36%), H-11->L+1 (20%), H-11->L+2 (-13%)
69	41414.44	241.461695	0.0012	Singlet-A	H-13->LUMO (34%), H-11->L+1 (-11%), H-11->L+2 (-18%)

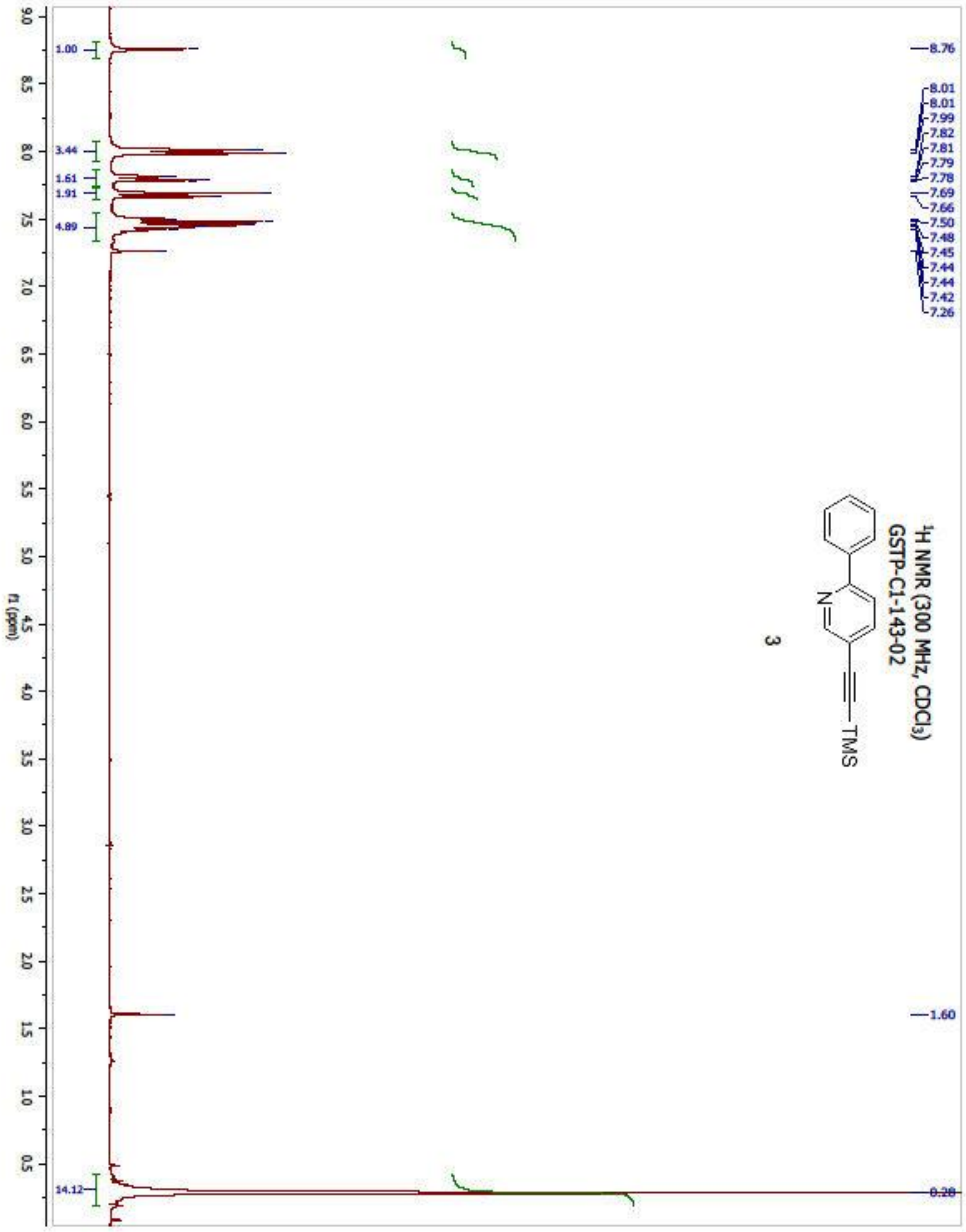
70	41508	240.917429	0.0039	Singlet-A	H-6->L+3 (77%)
71	41515.26	240.875304	0.0036	Singlet-A	H-7->L+3 (79%)
72	41824.98	239.091593	0.0744	Singlet-A	H-2->L+10 (23%), H-1->L+9 (-22%)
73	41830.62	239.059323	0.0746	Singlet-A	H-2->L+9 (22%), H-1->L+10 (23%)
74	41904.82	238.636005	0.0004	Singlet-A	H-13->L+1 (25%), H-13->L+2 (17%), H-12->L+1 (-18%), H-12->L+2 (25%)
75	42361.34	236.064311	0.0013	Singlet-A	H-13->L+2 (23%), H-12->L+1 (24%), H-8->L+4 (27%)
76	42367.79	236.028359	0.0014	Singlet-A	H-13->L+1 (23%), H-12->L+2 (-25%), H-8->L+5 (26%)
77	42485.55	235.374156	0.1383	Singlet-A	H-2->L+9 (13%), H-1->L+10 (-14%), HOMO->L+11 (43%)
78	42558.94	234.968231	0.0565	Singlet-A	H-13->L+1 (15%), H-13->L+2 (-18%), H-12->L+1 (32%), H-12->L+2 (20%)
79	42582.34	234.839164	0.004	Singlet-A	H-13->L+2 (-19%), H-8->L+4 (51%)
80	42586.37	234.816925	0.004	Singlet-A	H-13->L+1 (-18%), H-8->L+5 (52%)
81	42860.6	233.314521	0.002	Singlet-A	H-7->L+5 (21%), H-7->L+6 (-19%), H-6->L+4 (23%), H-6->L+7 (19%)
82	43043.69	232.322103	0.0293	Singlet-A	H-9->L+3 (53%), H-7->L+5 (-11%), H-6->L+4 (11%)
83	43047.72	232.300338	0.0292	Singlet-A	H-10->L+3 (52%), H-7->L+4 (11%), H-6->L+5 (13%)
84	43179.19	231.593045	0.0105	Singlet-A	H-7->L+4 (-35%), H-6->L+5 (37%)
85	43282.43	231.040636	0.0012	Singlet-A	H-9->L+3 (23%), H-7->L+5 (35%), H-6->L+4 (-34%)
86	43285.66	231.023416	0.0012	Singlet-A	H-10->L+3 (-24%), H-7->L+4 (35%), H-6->L+5 (33%)
87	43526.82	229.743425	0.028	Singlet-A	H-7->L+5 (-10%), H-7->L+6 (-19%), H-6->L+7 (19%)
88	43923.64	227.667811	0.0994	Singlet-A	HOMO->L+11 (33%)
89	44201.91	226.23458	0.0005	Singlet-A	H-11->L+3 (45%), H-10->L+5 (10%), H-9->L+4 (-11%)
90	44219.65	226.143797	0.0123	Singlet-A	H-2->L+11 (31%), H-1->L+11 (34%)
91	44222.88	226.127299	0.0133	Singlet-A	H-2->L+11 (33%), H-1->L+11 (-32%)
92	44471.3	224.864132	0.0591	Singlet-A	HOMO->L+12 (39%), HOMO->L+14 (-17%)
93	44481.78	224.811127	0.0582	Singlet-A	HOMO->L+13 (38%), HOMO->L+15 (18%)
94	44678.58	223.820877	0.0016	Singlet-A	H-11->L+3 (22%), H-10->L+4 (10%), H-9->L+5 (29%)
95	44682.62	223.800676	0.0013	Singlet-A	H-10->L+4 (28%)
96	44685.04	223.788558	0.0014	Singlet-A	H-10->L+5 (17%), H-9->L+4 (18%)
97	44870.55	222.863346	0.015	Singlet-A	H-10->L+5 (12%), H-9->L+4 (13%), HOMO->L+13 (19%), HOMO->L+15 (-10%)
98	44873.77	222.847323	0.015	Singlet-A	H-10->L+4 (12%), H-9->L+5 (-12%), HOMO->L+12 (20%), HOMO->L+14 (11%)
99	44952.82	222.455479	0.006	Singlet-A	H-4->L+7 (20%), H-3->L+6 (48%)
100	44984.27	222.299924	0.0056	Singlet-A	H-4->L+6 (39%), H-3->L+7 (33%)

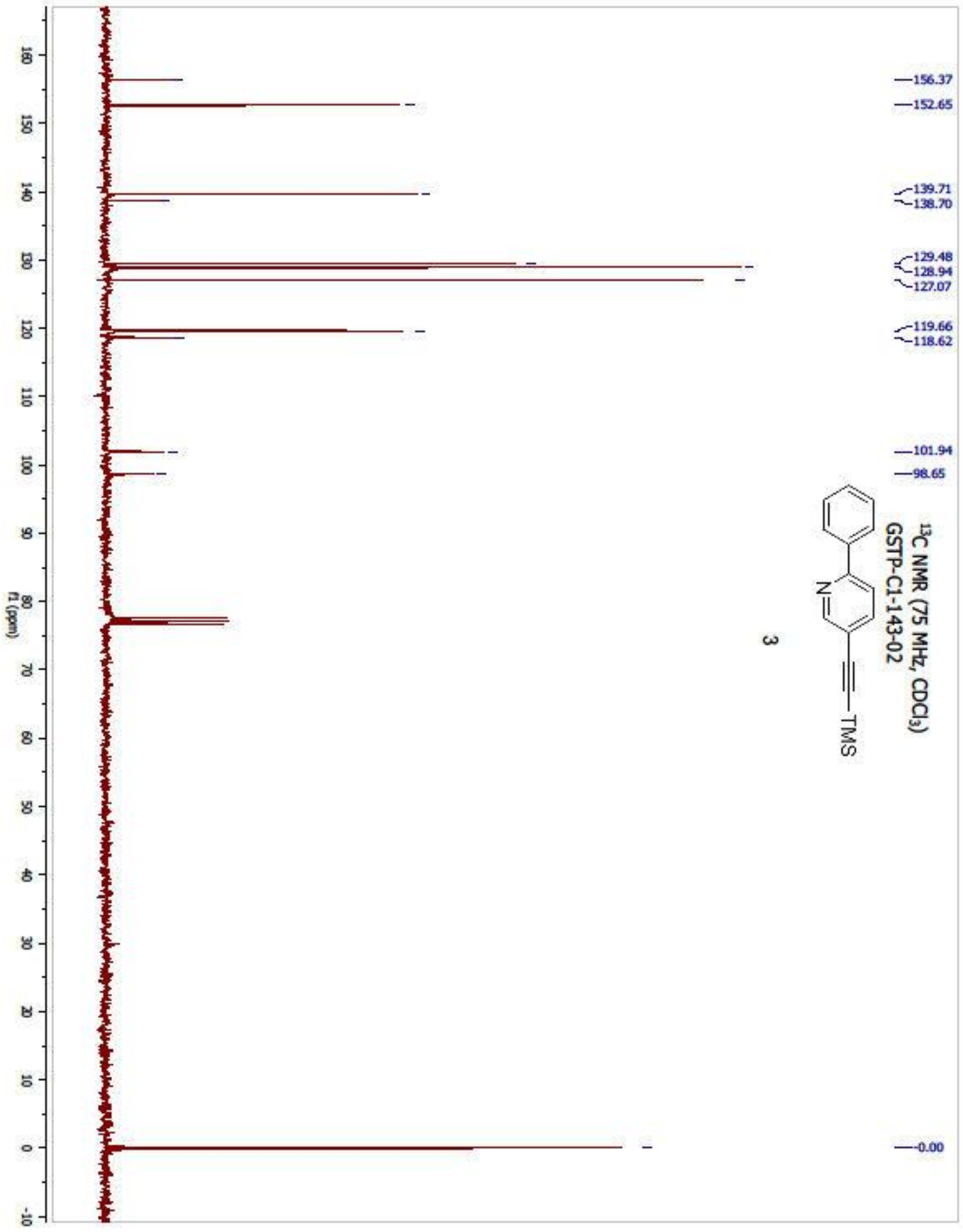
NMR characterization.




^1H NMR (300 MHz, $CDCl_3$)
GSTP-C1-054-01
2
N
Br
8.74
8.74
7.97
7.97
7.95
7.94
7.89
7.89
7.87
7.86
7.65
7.62
7.50
7.48
7.46
7.43
7.26
1.56
0.70
2.19
1.00
1.21
3.24
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
f1 (ppm)

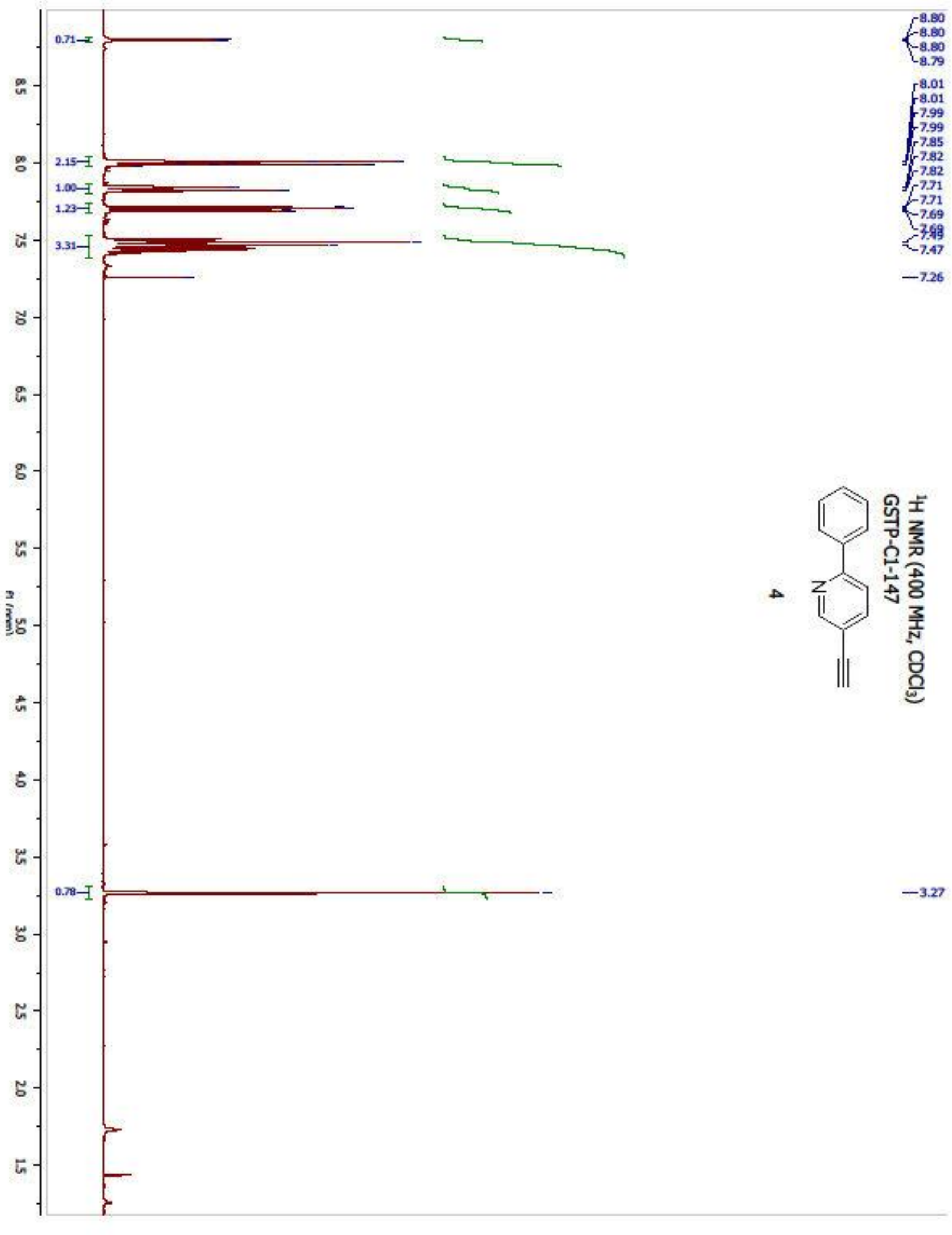

156.02
150.81
139.41
129.47
128.99
126.88
121.76
119.44
^{13}C NMR (75 MHz, CDCl$_3$)
GSTP-C1-054-01
N
Br
2
160
155
150
145
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
f1 (ppm)


¹H NMR (300 MHz, CDCl₃)
GSTP-C1-143-02
3
N
TMS
8.76
8.01
8.01
7.99
7.82
7.81
7.79
7.78
7.69
7.66
7.50
7.48
7.45
7.44
7.44
7.42
7.26
1.60
0.28
1.00
3.44
1.61
1.91
4.89
14.12
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)



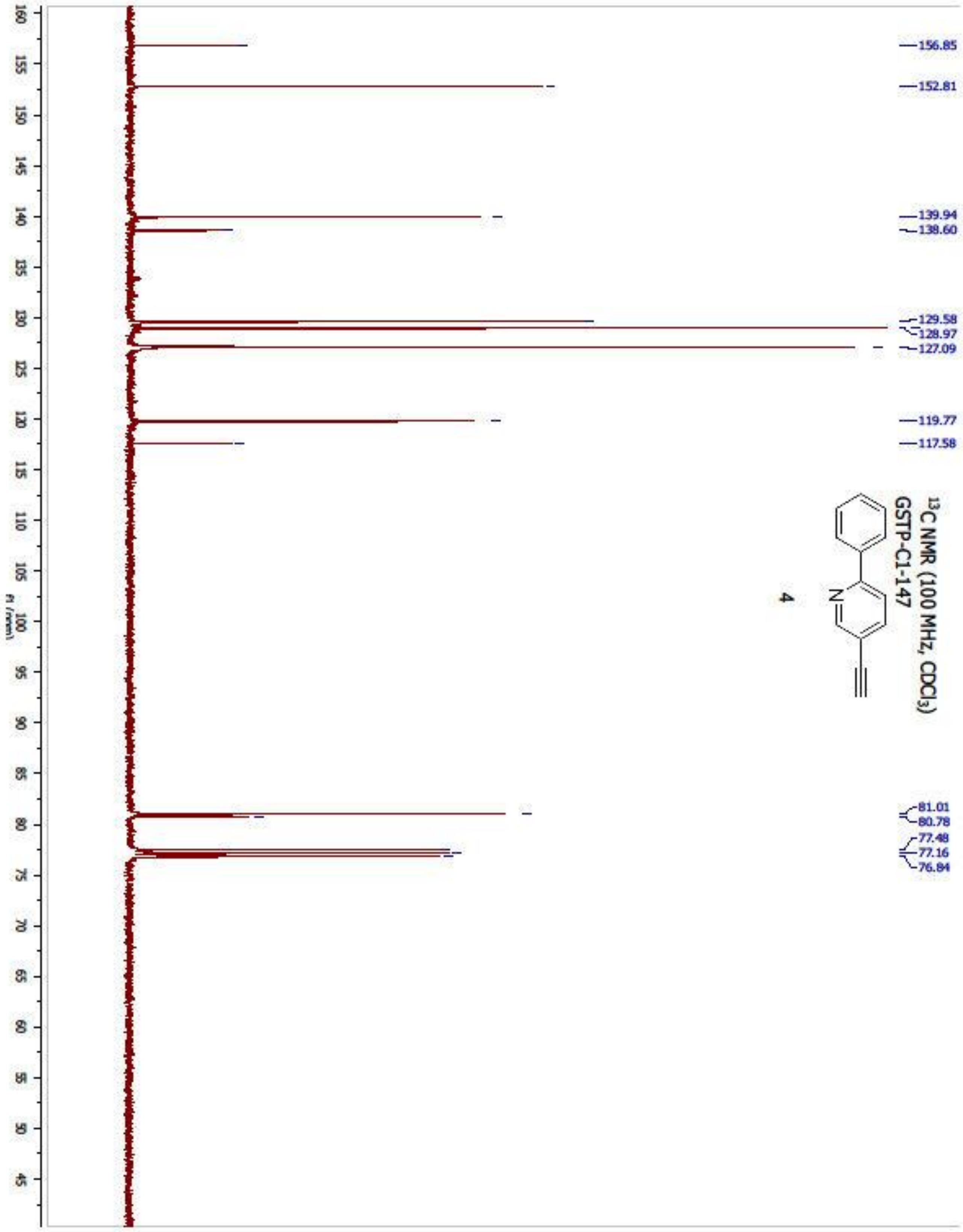
^{13}C NMR (75 MHz, CDCl$_3$)
GSTP-C1-143-02

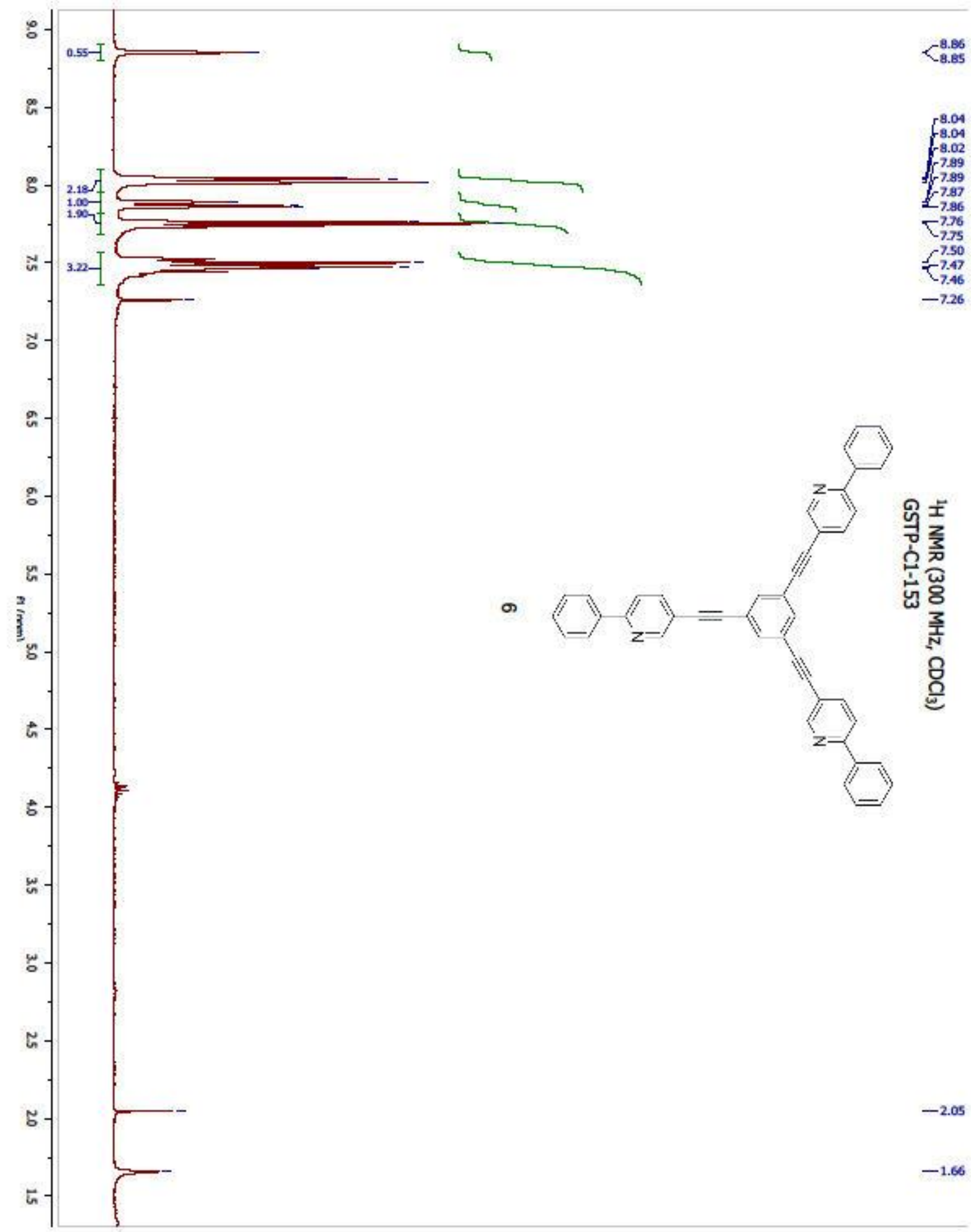
3

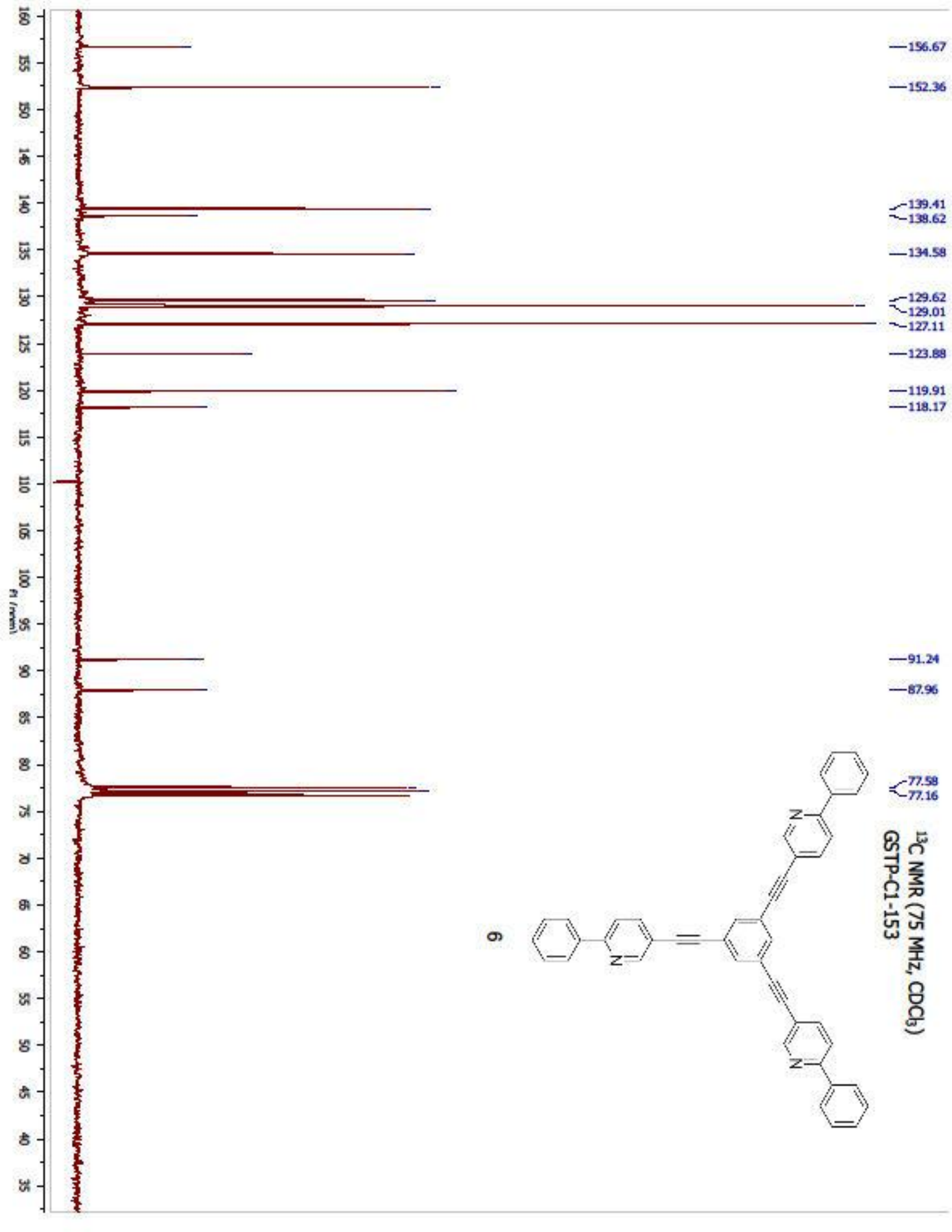


^{1}H NMR (400 MHz, CDCl$_3$)
GSTP-C1-147

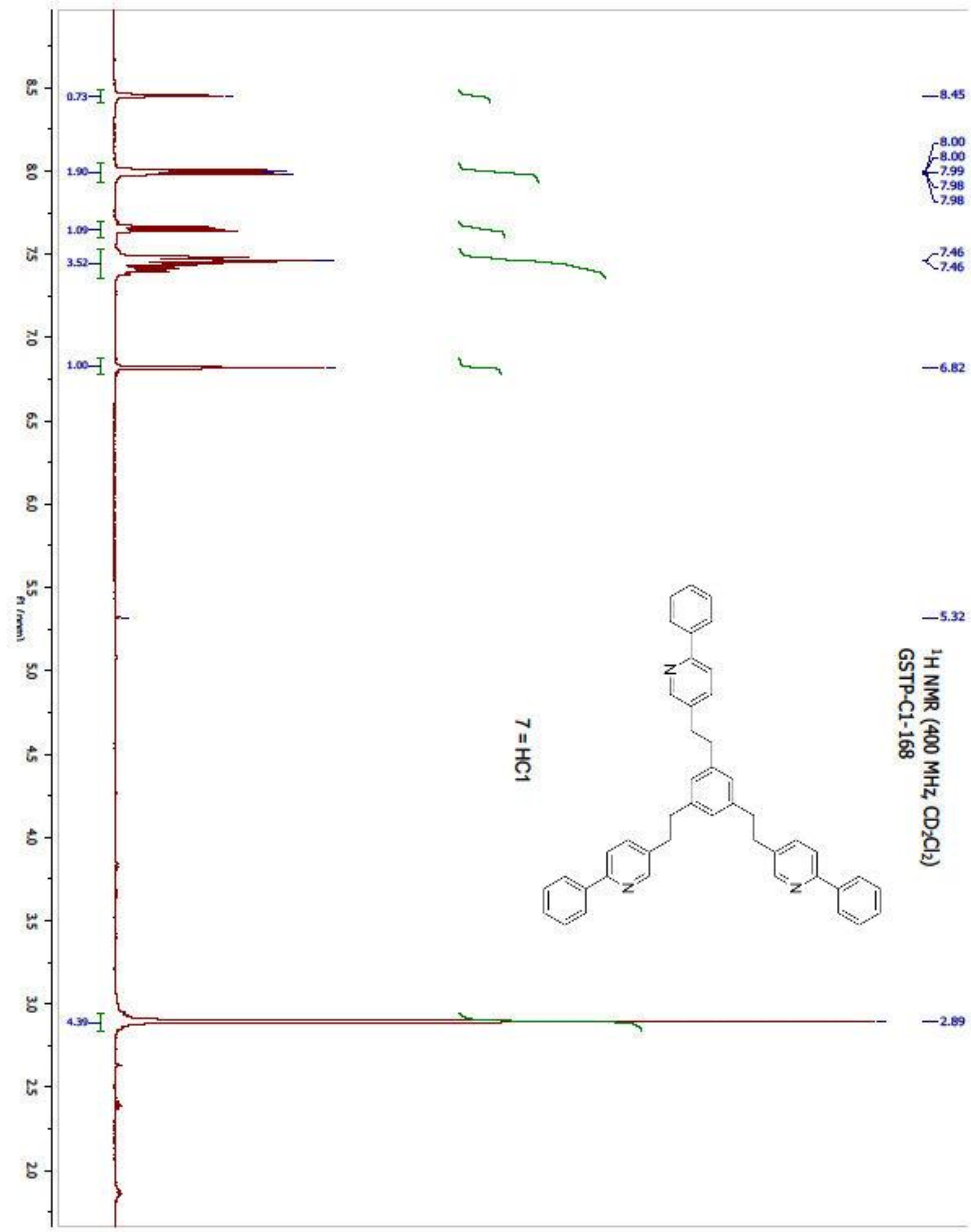
4


^{13}C NMR (100 MHz, CDCl$_3$)
GSTP-C1-147
4
N
156.85
152.81
139.94
138.60
129.58
128.97
127.09
119.77
117.58
81.01
80.78
77.48
77.16
76.84
160
155
150
145
140
135
130
125
120
115
110
105
100
f1 (ppm)
95
90
85
80
75
70
65
60
55
50
45


^{1}H NMR (300 MHz, $CDCl_3$)
GSTP-C1-153
6
N
N
N
8.86
8.85
8.04
8.04
8.02
7.89
7.89
7.87
7.86
7.76
7.75
7.50
7.47
7.46
7.26
2.05
1.66
0.55
2.18
1.00
1.90
3.22
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
f1 (ppm)

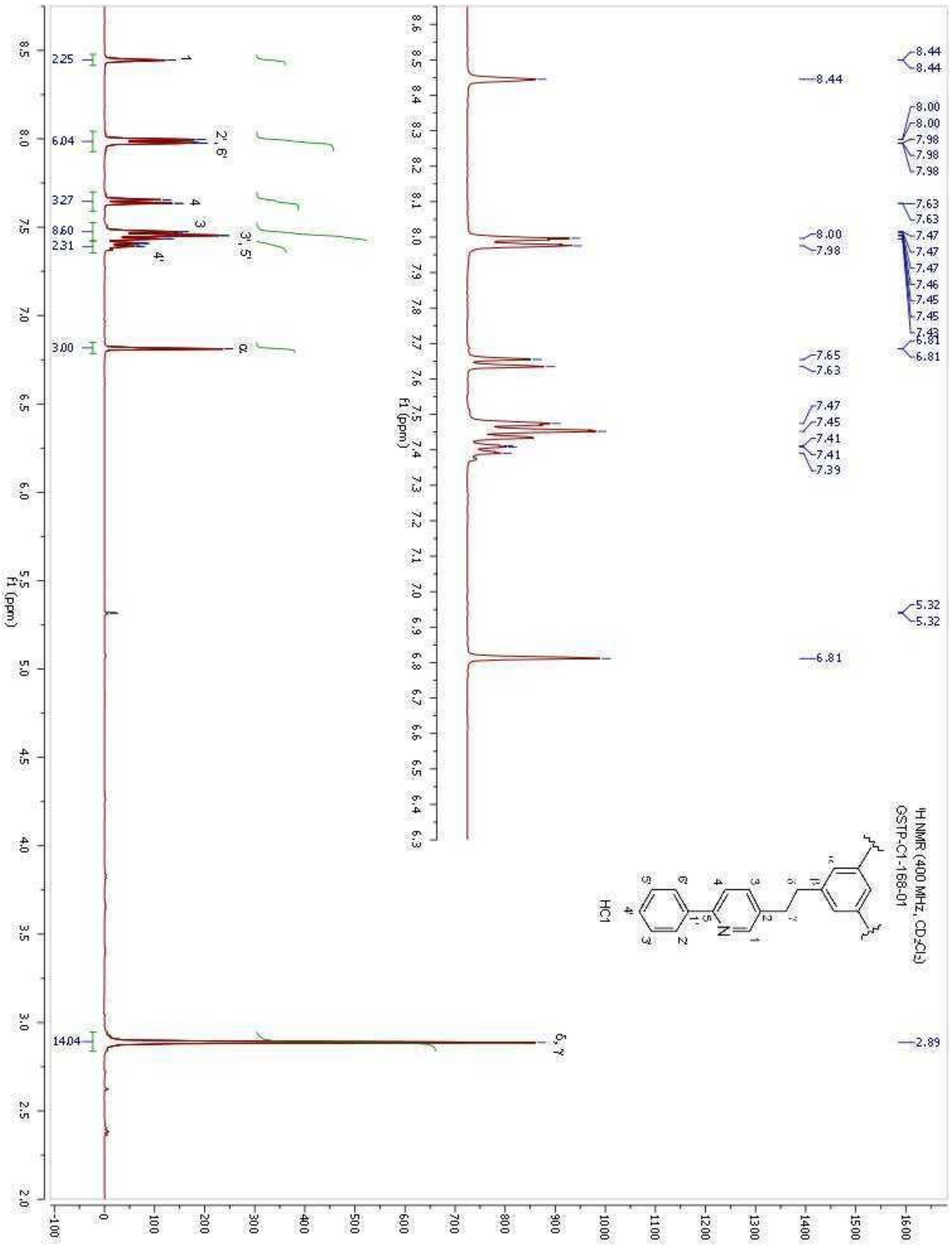

160
155
150
145
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
f1 (ppm)
156.67
152.36
139.41
138.62
134.58
129.62
129.01
127.11
123.88
119.91
118.17
91.24
87.96
77.58
77.16
N
N
N
^{13}C NMR (75 MHz, CDCl$_3$)
GSTP-C1-153

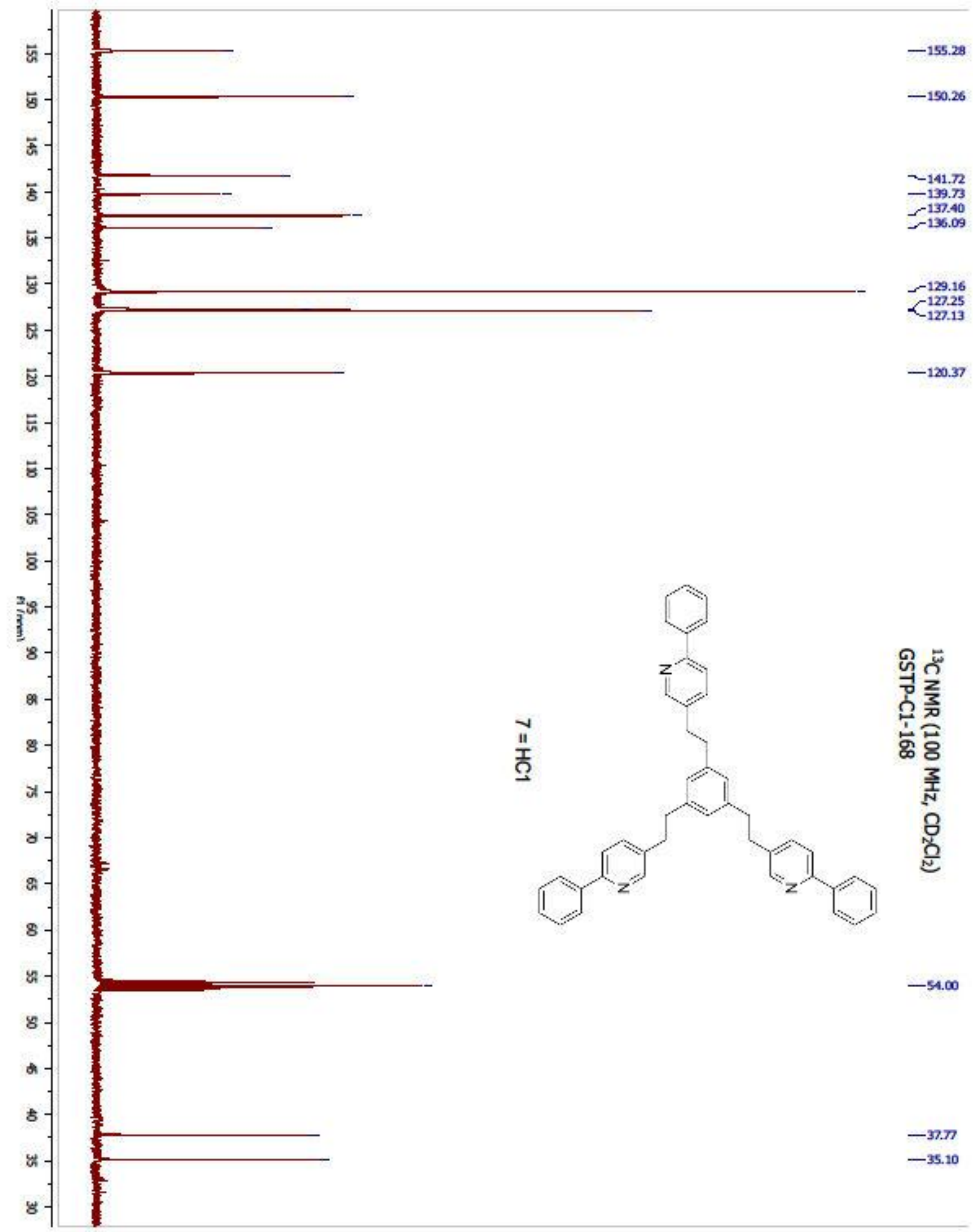
6



^{1}H NMR (400 MHz, CD_2Cl_2)
GSTP-C1-168

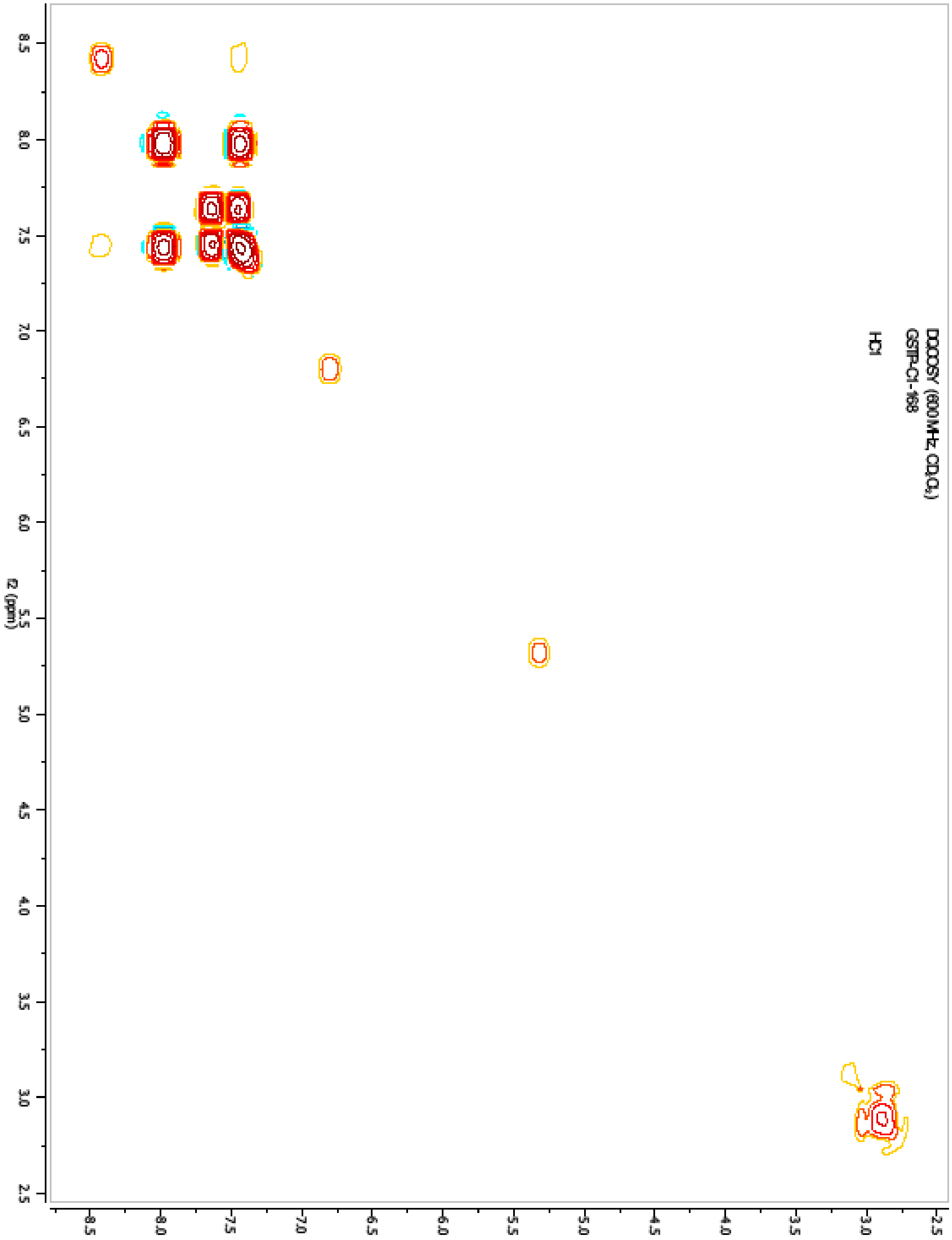
7 = HC1

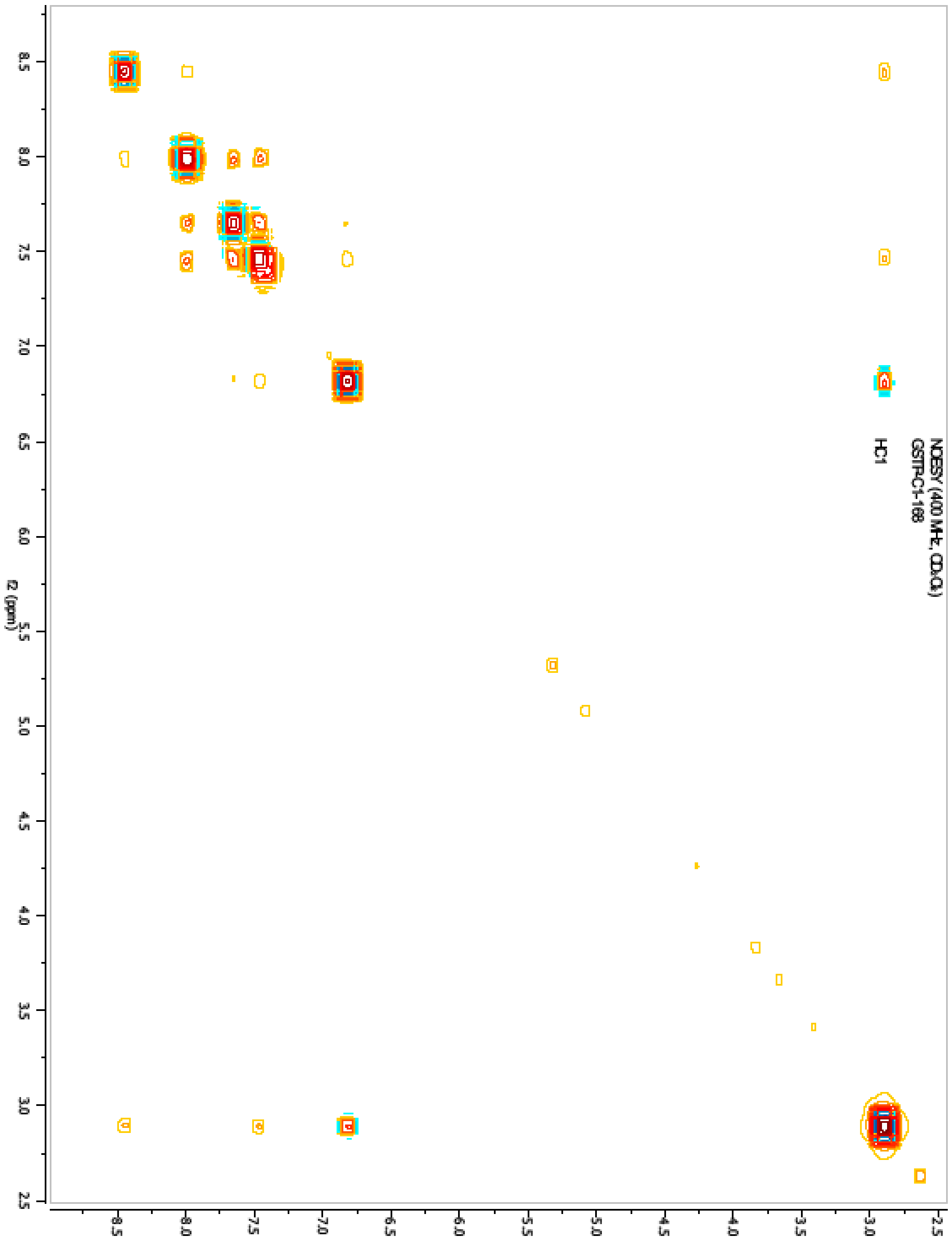

¹H NMR (400 MHz, CD₂Cl₂)
GSTP-C1-168-01
HCl
1
2
3
4
5
6
1'
2'
3'
4'
5'
6'
α
β
γ
δ
N
8.44
8.44
8.00
8.00
7.98
7.98
7.98
7.63
7.63
7.47
7.47
7.47
7.46
7.45
7.45
7.43
6.81
6.81
5.32
5.32
2.89
8.44
8.00
7.98
7.65
7.63
7.47
7.45
7.41
7.41
7.39
6.81
2.25
6.04
3.27
8.60
2.31
3.00
14.04
1
2',6'
4
3
3',5'
4'
α
δ, γ
f1 (ppm)
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
8.6
8.4
8.3
8.2
8.1
7.9
7.8
7.7
7.6
7.4
7.3
7.2
7.1
6.9
6.8
6.7
6.6
6.5
6.4
6.3
-100
0
100
200
300
400
500
600
700
800
900
1000
1100
1200
1300
1400
1500
1600

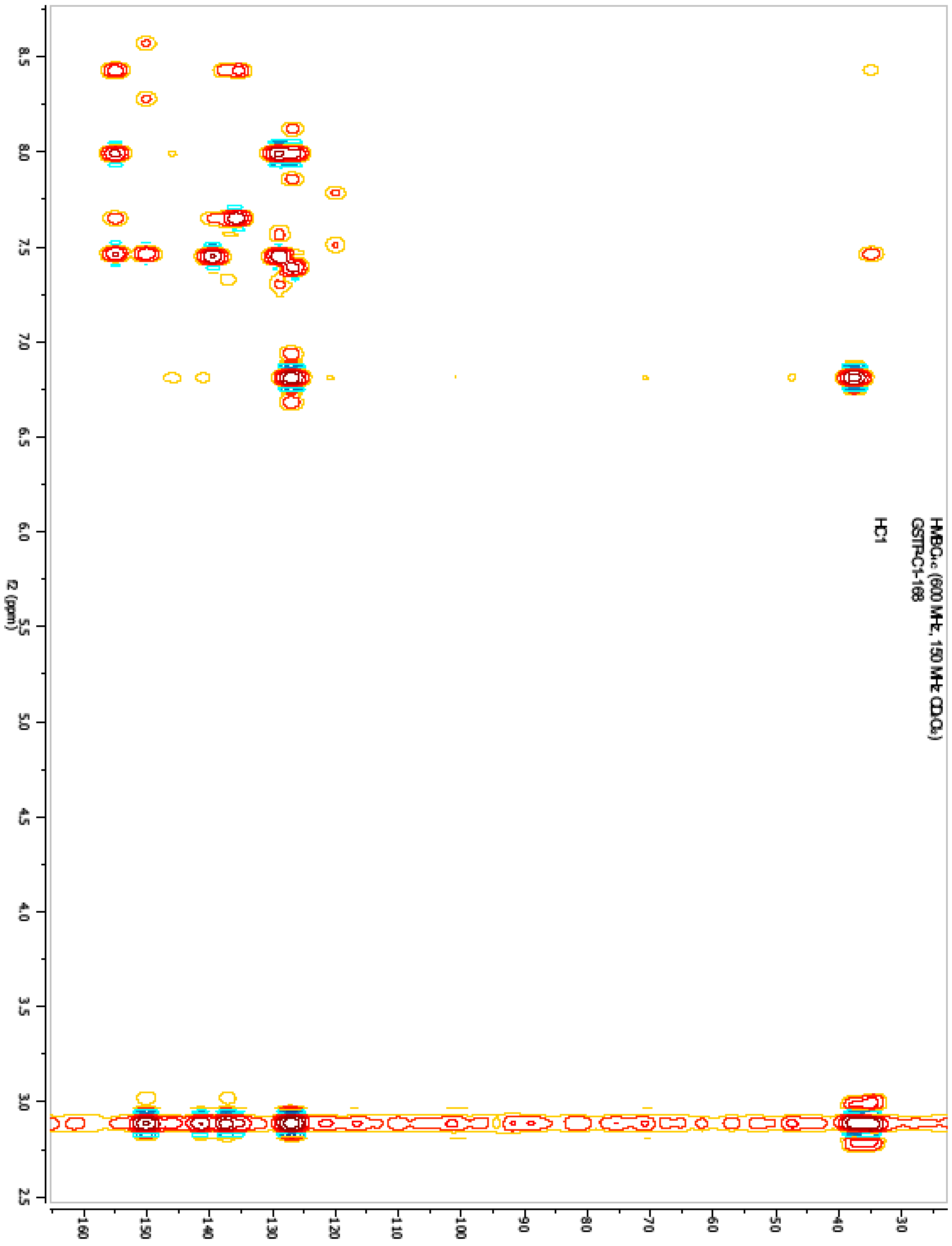


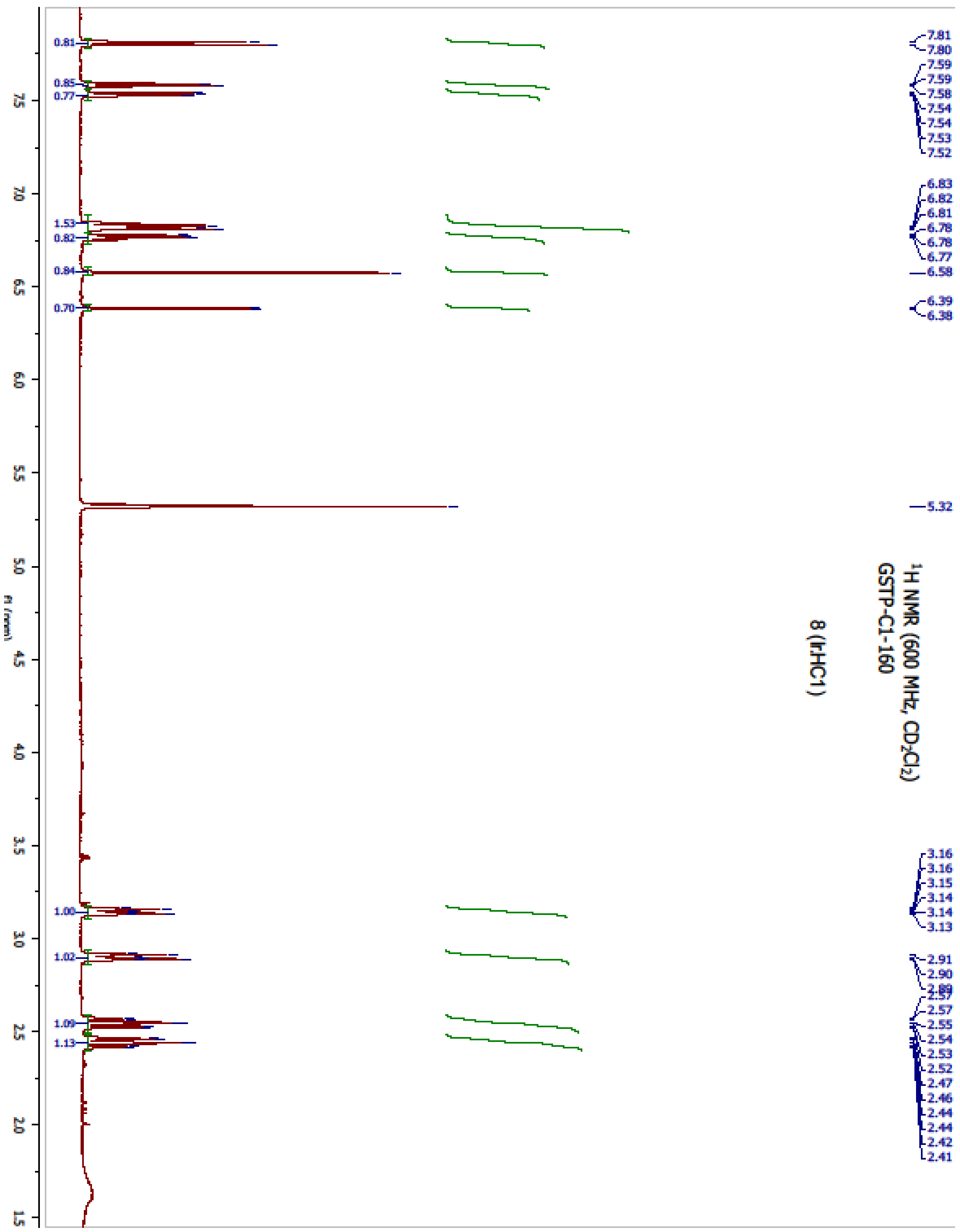
^{13}C NMR (100 MHz, CD_2Cl_2)
GSTP-C1-168

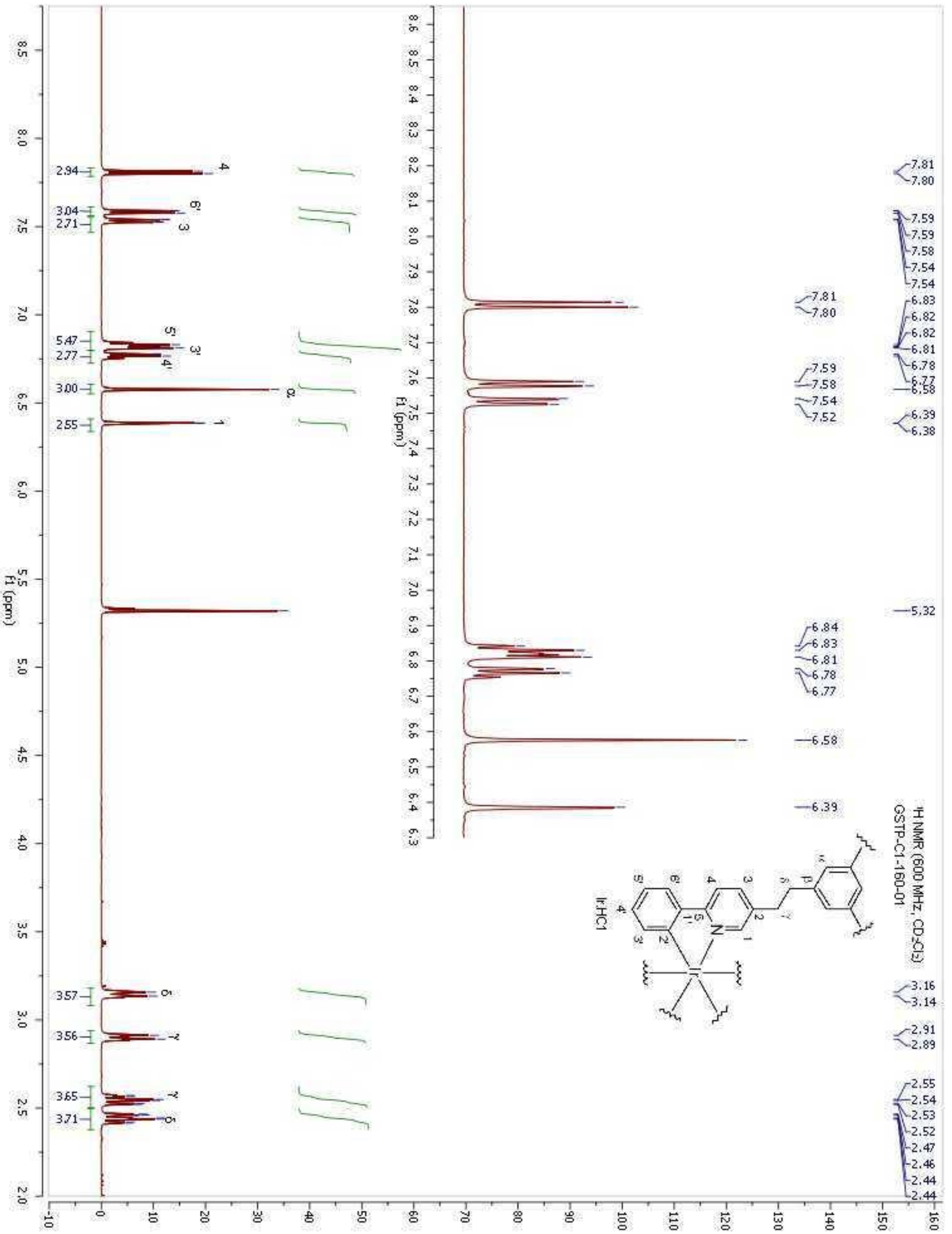
7 = HCl

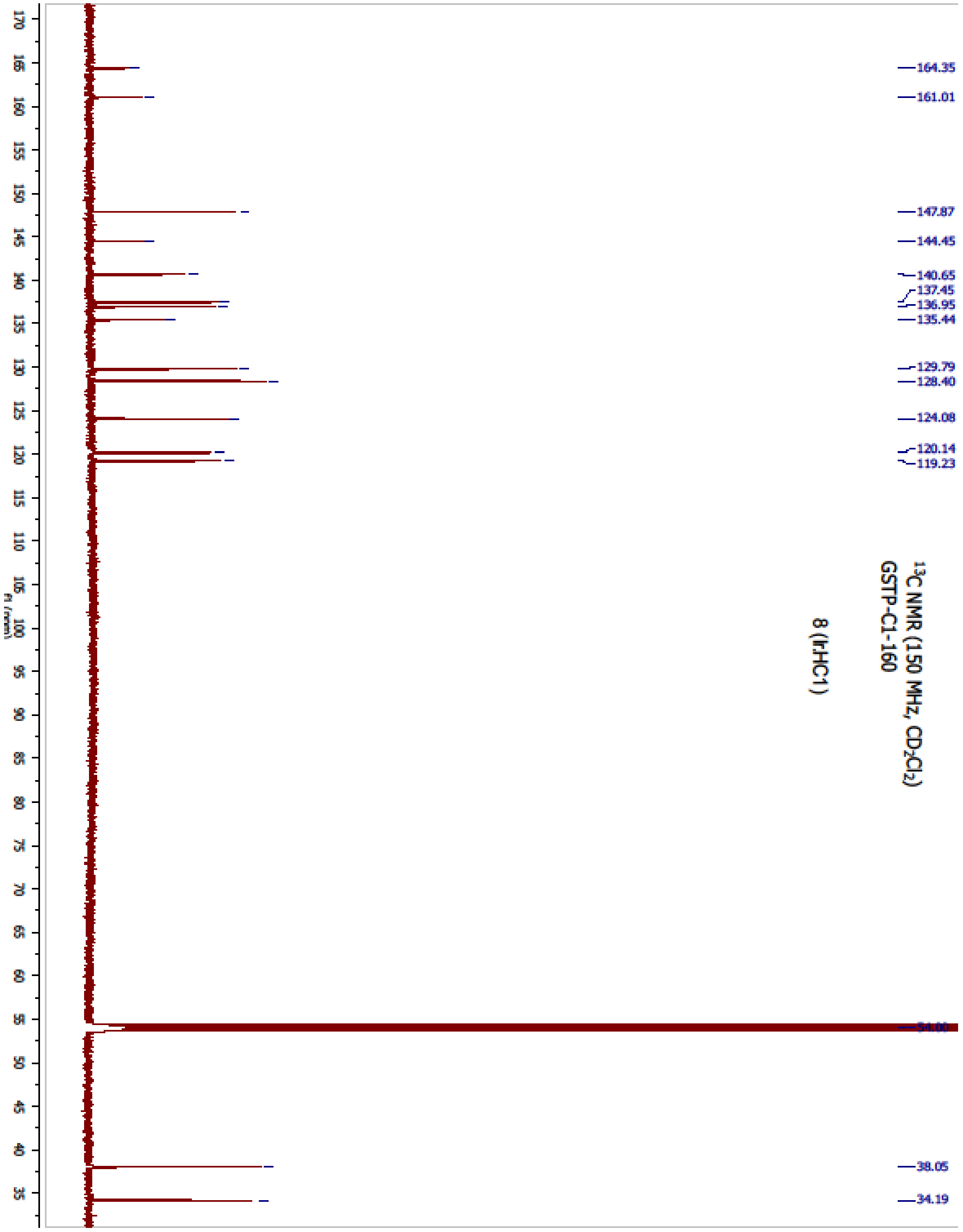

DQCOSY (600 MHz, CD$_2$Cl$_2$)
GSTP-C1-168
HCl
f2 (ppm)
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5

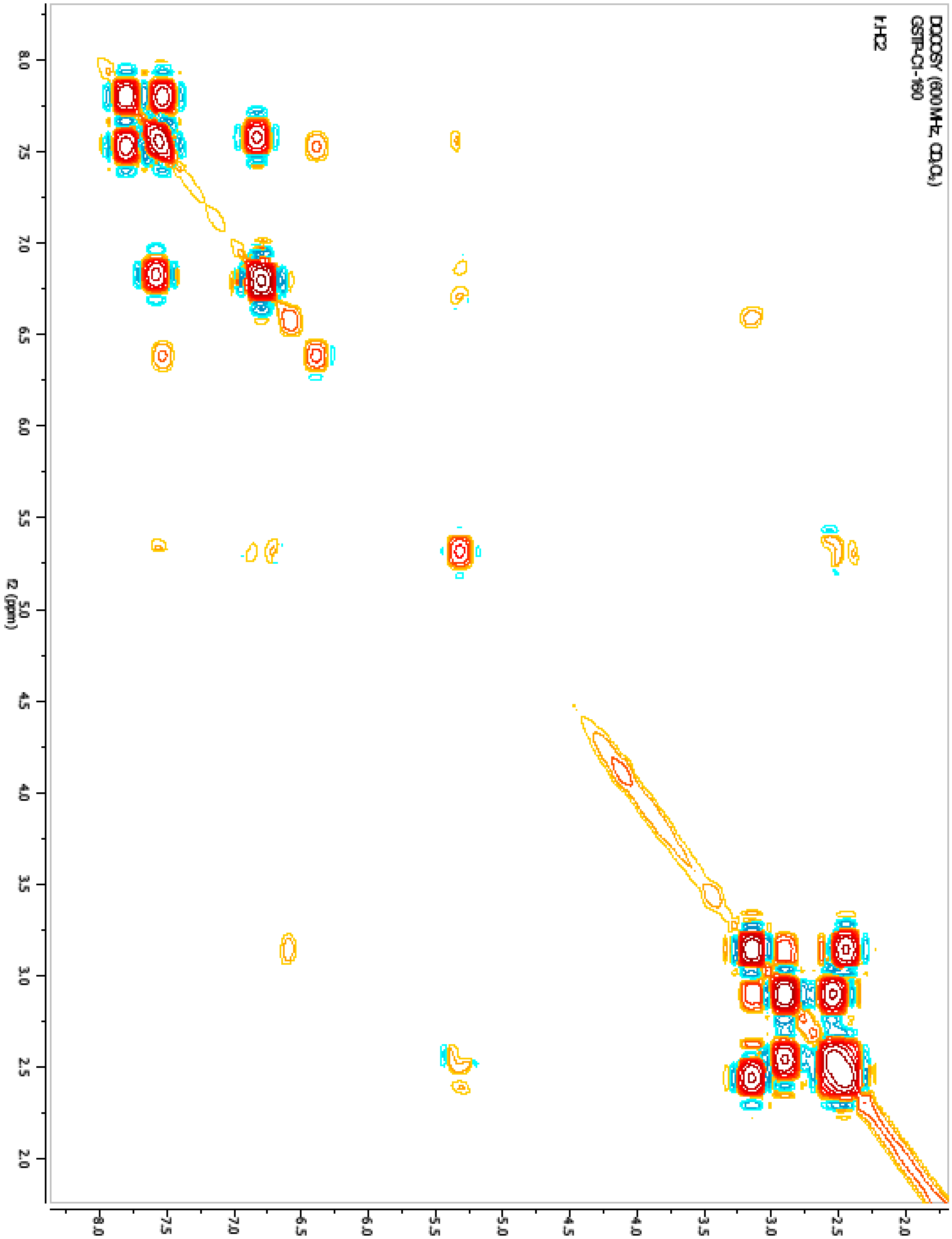

NOESY (400 MHz, CD2Cl2)
GSTP-C1-168
HC1
f2 (ppm)
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5

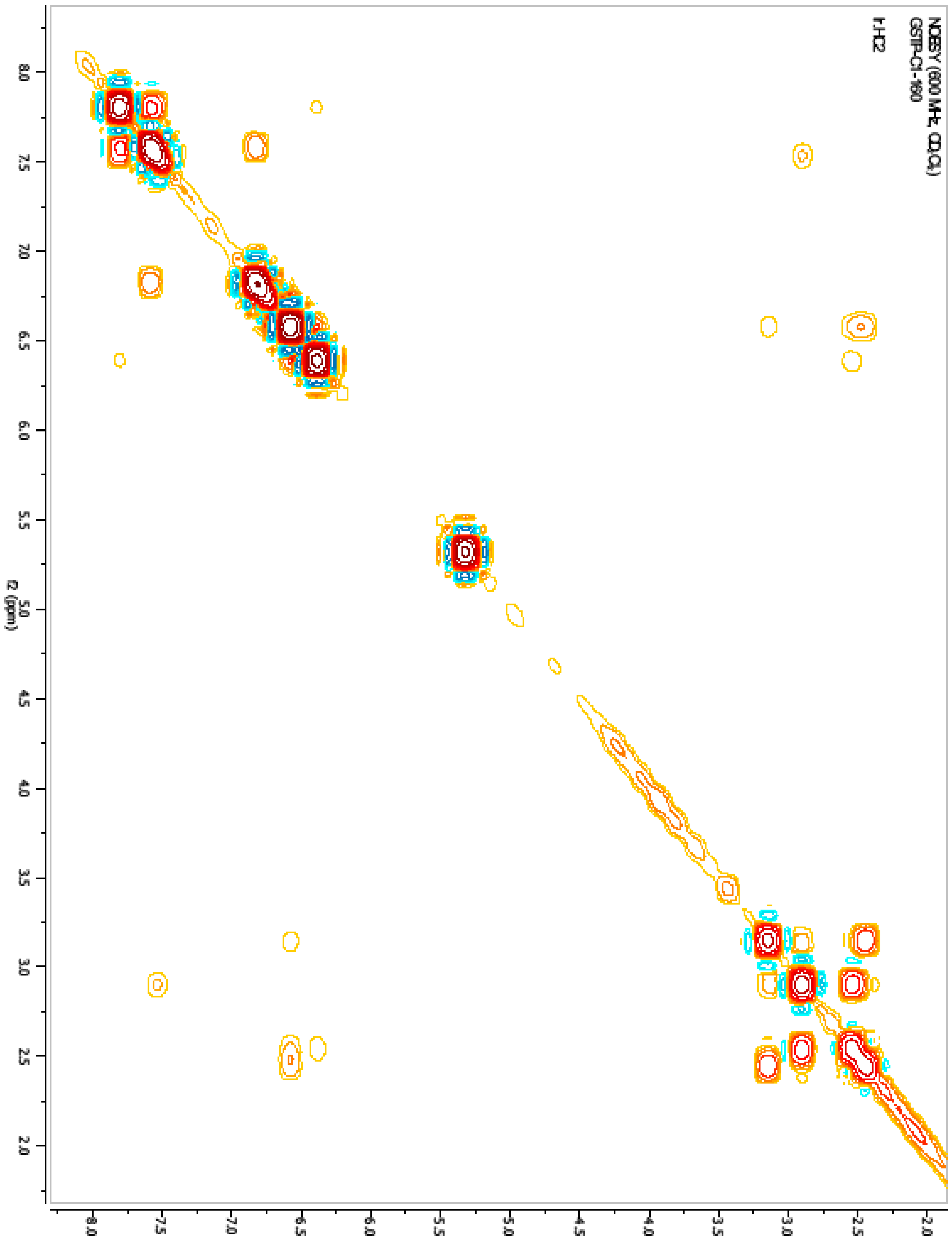

HMBC$_{H-C}$ (600 MHz, 150 MHz CD$_2$Cl$_2$)
GSTP-C1-168
HC1
f2 (ppm)
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
160
150
140
130
120
110
100
90
80
70
60
50
40
30

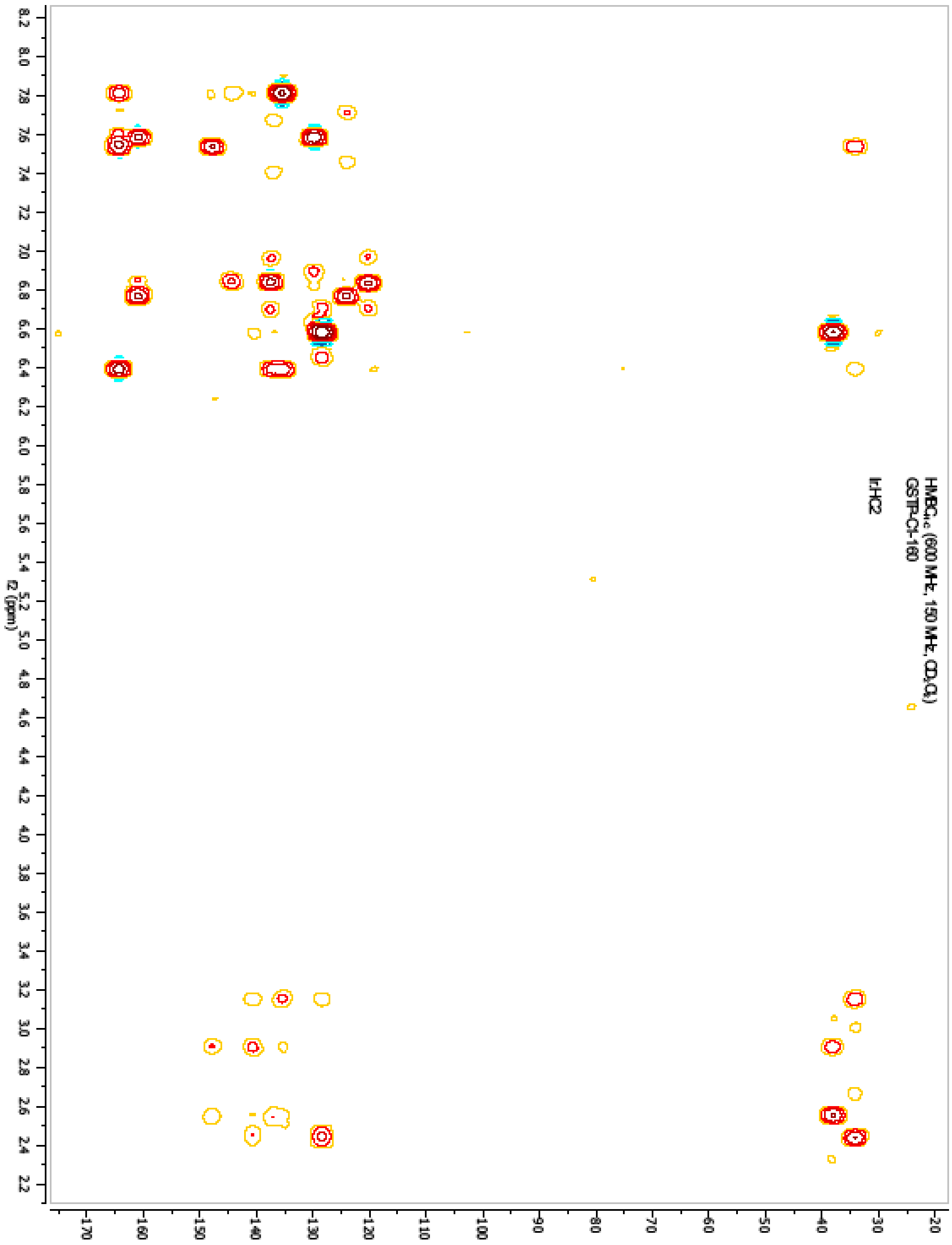

1H NMR (600 MHz, CD2Cl2)
GSTP-C1-160
8 (IrHCl)
7.81
7.80
7.59
7.59
7.58
7.54
7.54
7.53
7.52
6.83
6.82
6.81
6.78
6.78
6.77
6.58
6.39
6.38
5.32
3.16
3.16
3.15
3.14
3.14
3.13
2.91
2.90
2.89
2.57
2.57
2.55
2.54
2.53
2.52
2.47
2.46
2.44
2.44
2.42
2.41
0.81
0.85
0.77
1.53
0.82
0.84
0.70
1.00
1.02
1.09
1.13
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
f1 (ppm)

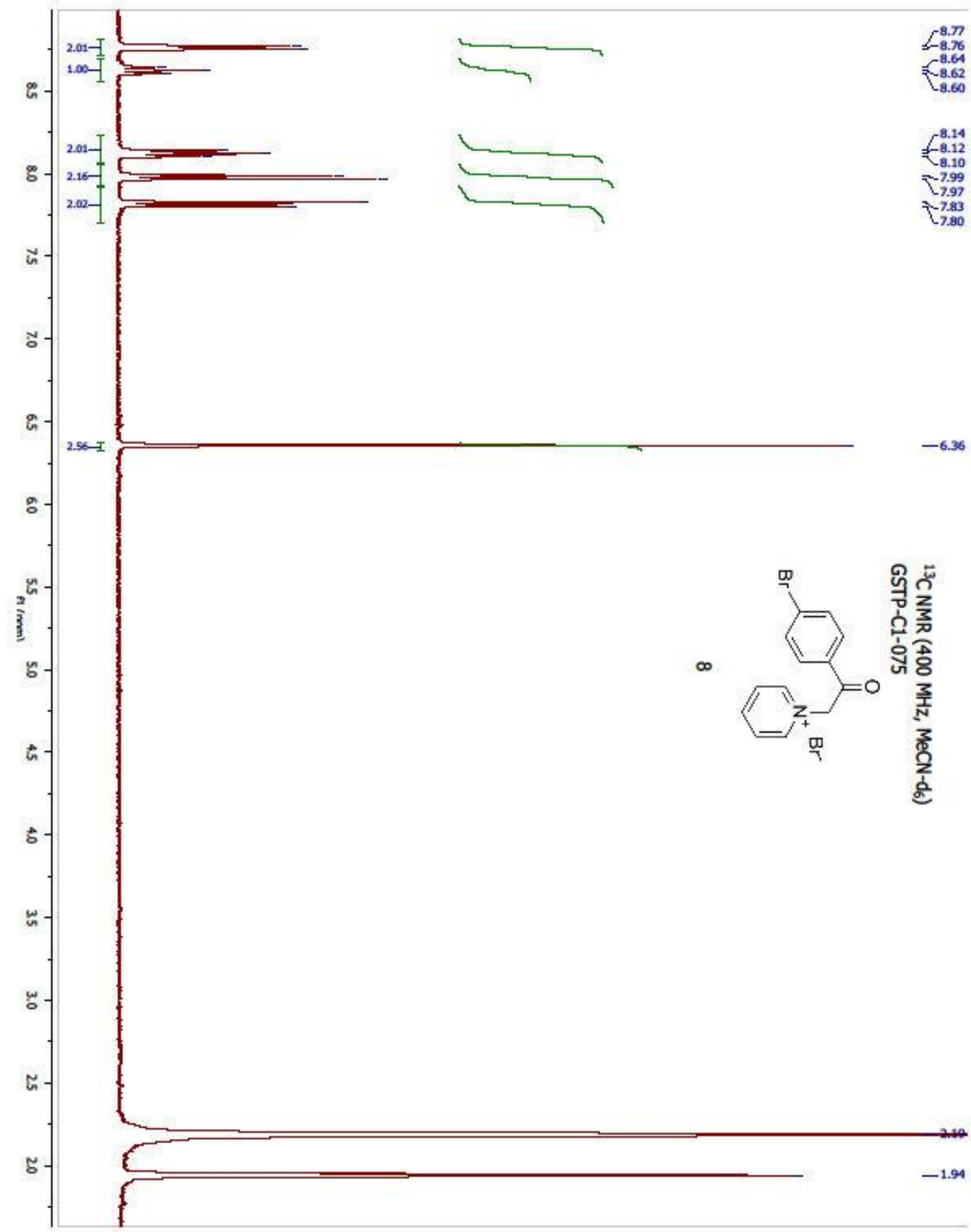

1H NMR (600 MHz, CD2Cl2)
GSTP-C1-160-01
Ir.HC1
7.81
7.80
7.59
7.59
7.58
7.54
7.54
6.83
6.82
6.82
6.81
6.78
6.77
6.58
6.39
6.38
5.32
3.16
3.14
2.91
2.89
2.55
2.54
2.53
2.52
2.47
2.46
2.44
2.44
7.81
7.80
7.59
7.58
7.54
7.52
6.84
6.83
6.81
6.78
6.77
6.58
6.39
2.94
3.04
2.71
5.47
2.77
3.00
2.55
3.57
3.56
3.65
3.71
4
6'
3
5'
3'
4'
α
1
δ
γ
γ
δ
β
1'
2'
5
f1 (ppm)
f1 (ppm)

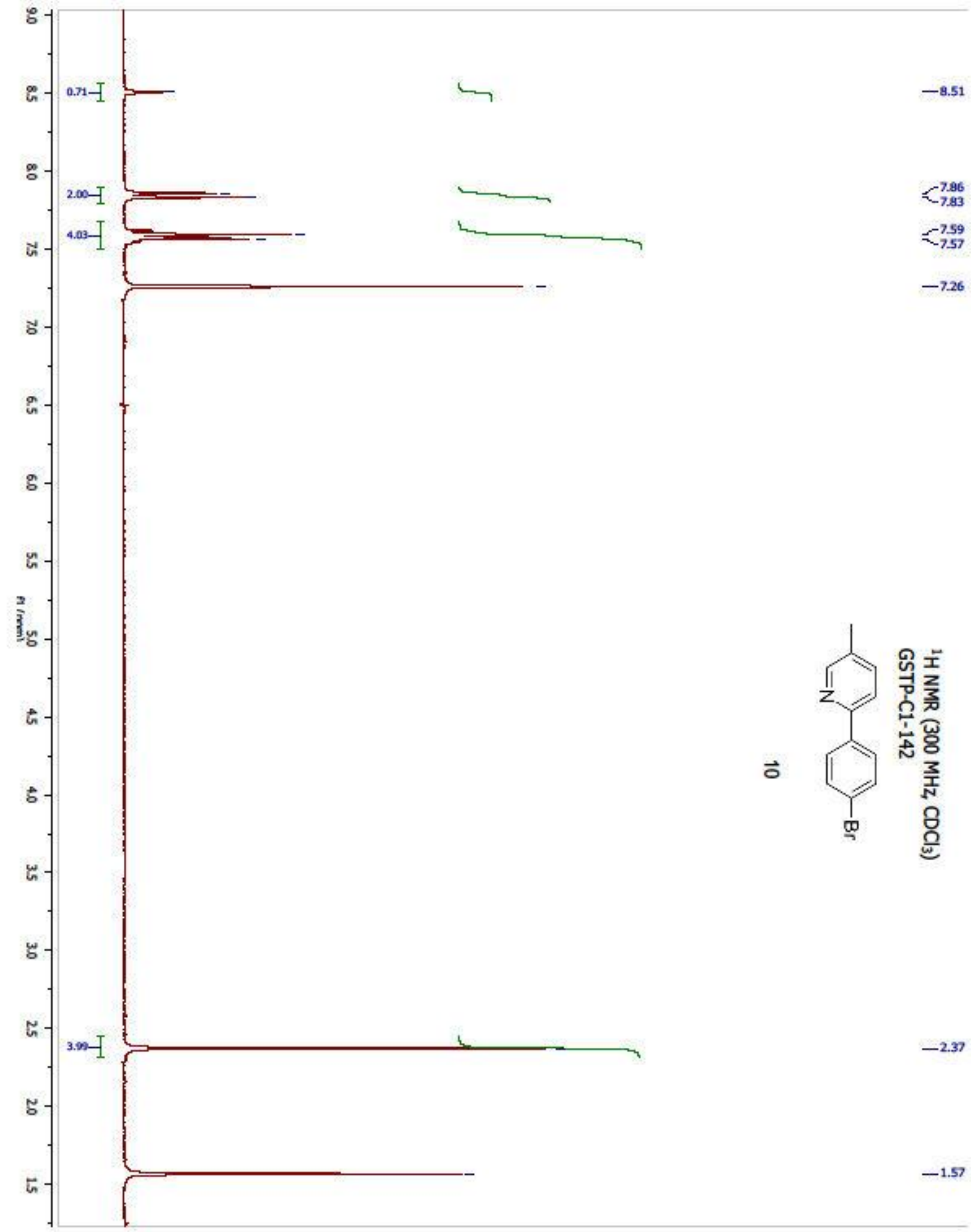

13C NMR (150 MHz, CD2Cl2)
GSTP-C1-160
8 (IrHC1)
164.35
161.01
147.87
144.45
140.65
137.45
136.95
135.44
129.79
128.40
124.08
120.14
119.23
54.00
38.05
34.19
f1 (ppm)
170
165
160
155
150
145
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35


DQCOSY (600 MHz, CD2Cl2)
GSTP-C1-160
f1:H2
f2 (ppm)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0

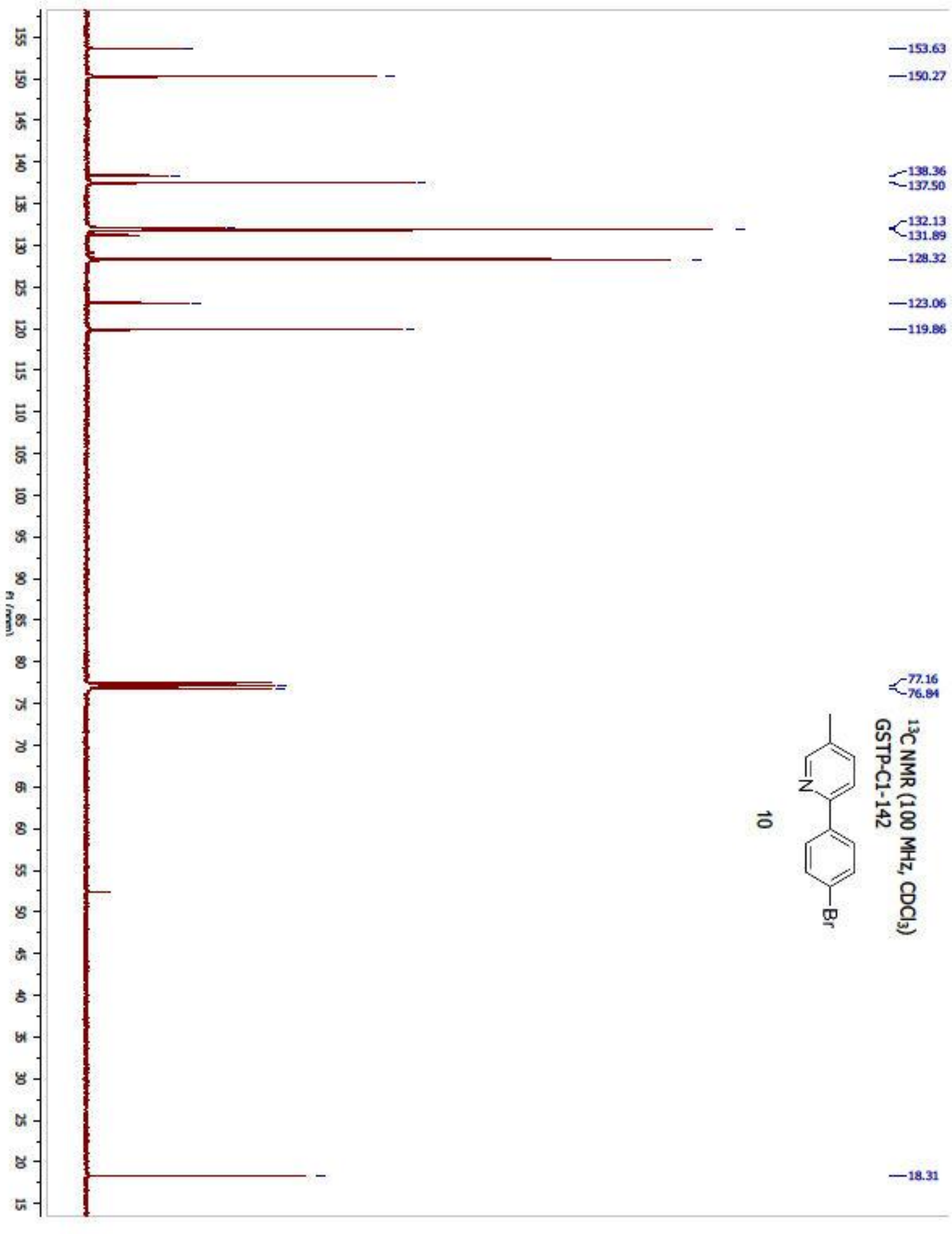

NOESY (600 MHz, CDCl3)
GSTP-C1-160
f1:H2
f2 (ppm)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0

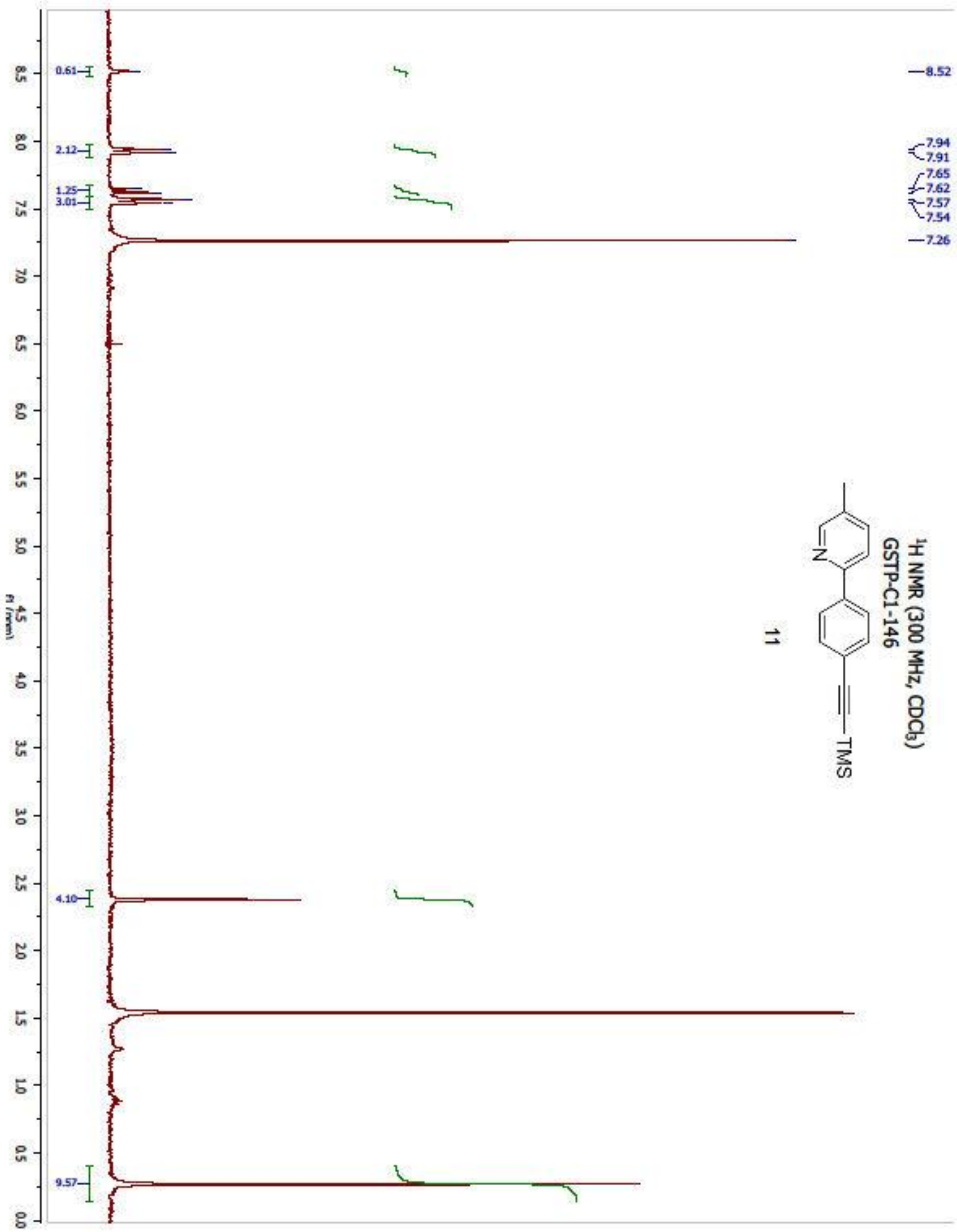

HMBC$_{H-C}$ (600 MHz, 150 MHz, CD$_2$Cl$_2$)
GSTP-C1-160
IrHC2
f2 (ppm)
8.2
8.0
7.8
7.6
7.4
7.2
7.0
6.8
6.6
6.4
6.2
6.0
5.8
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20

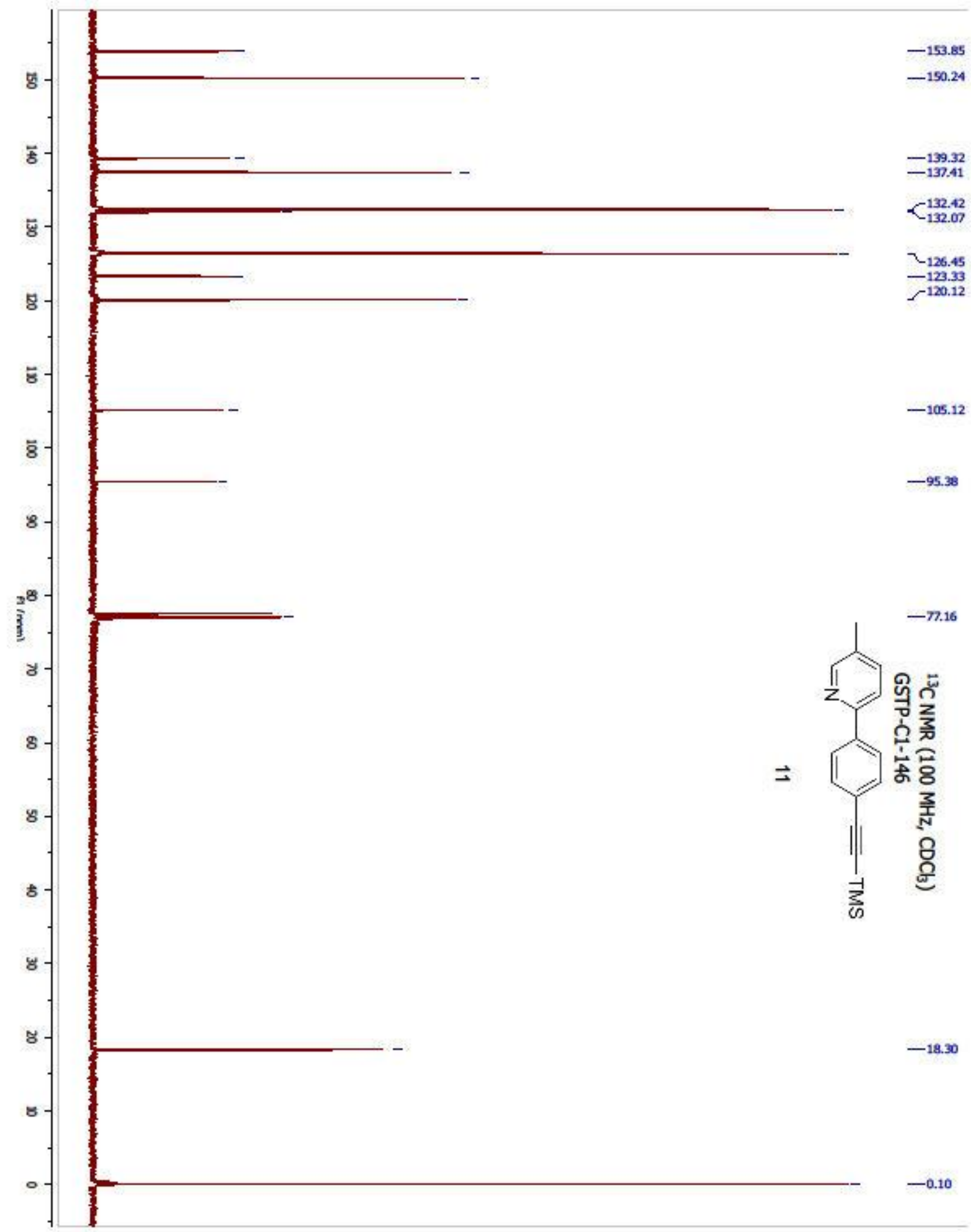

^{13}C NMR (400 MHz, MeCN-d_6)
GSTP-C1-075
8
O
N+
Br
Br-
8.77
8.76
8.64
8.62
8.60
8.14
8.12
8.10
7.99
7.97
7.83
7.80
6.36
2.19
1.94
2.01
1.00
2.01
2.16
2.02
2.56
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
f1 (ppm)


¹H NMR (300 MHz, CDCl₃)
GSTP-C1-142
N
Br
8.51
7.86
7.83
7.59
7.57
7.26
2.37
1.57
0.71
2.00
4.03
3.99
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
f1 (ppm)

10

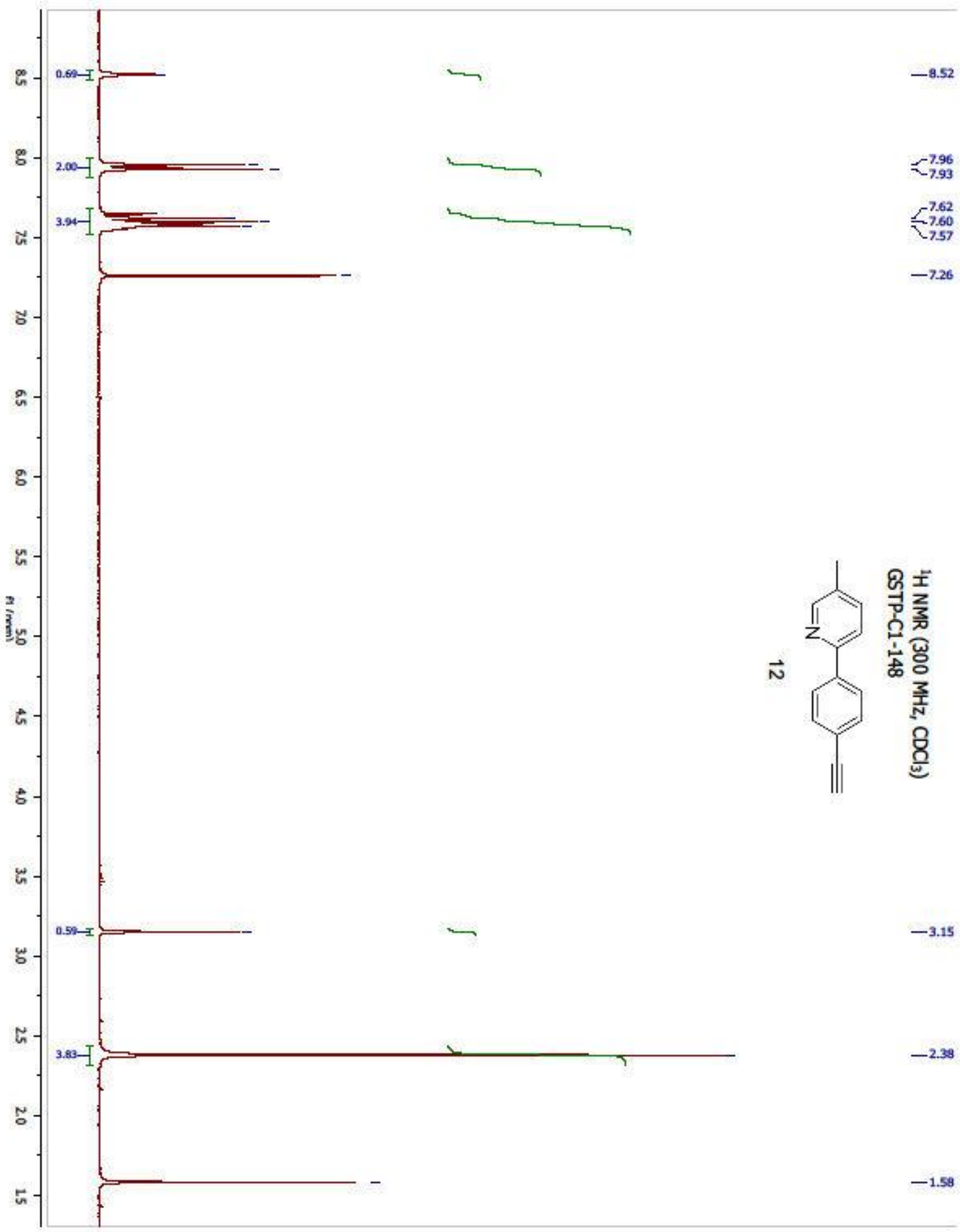

^{13}C NMR (100 MHz, CDCl$_3$)
GSTP-C1-142
10
N
Br
153.63
150.27
138.36
137.50
132.13
131.89
128.32
123.06
119.86
77.16
76.84
18.31
f1 (ppm)
155
150
145
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15


^{1}H NMR (300 MHz, CDCl$_3$)
GSTP-C1-146
11
N
TMS
8.52
7.94
7.91
7.65
7.62
7.57
7.54
7.26
0.61
2.12
1.25
3.01
4.10
9.57
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
f1 (ppm)
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0



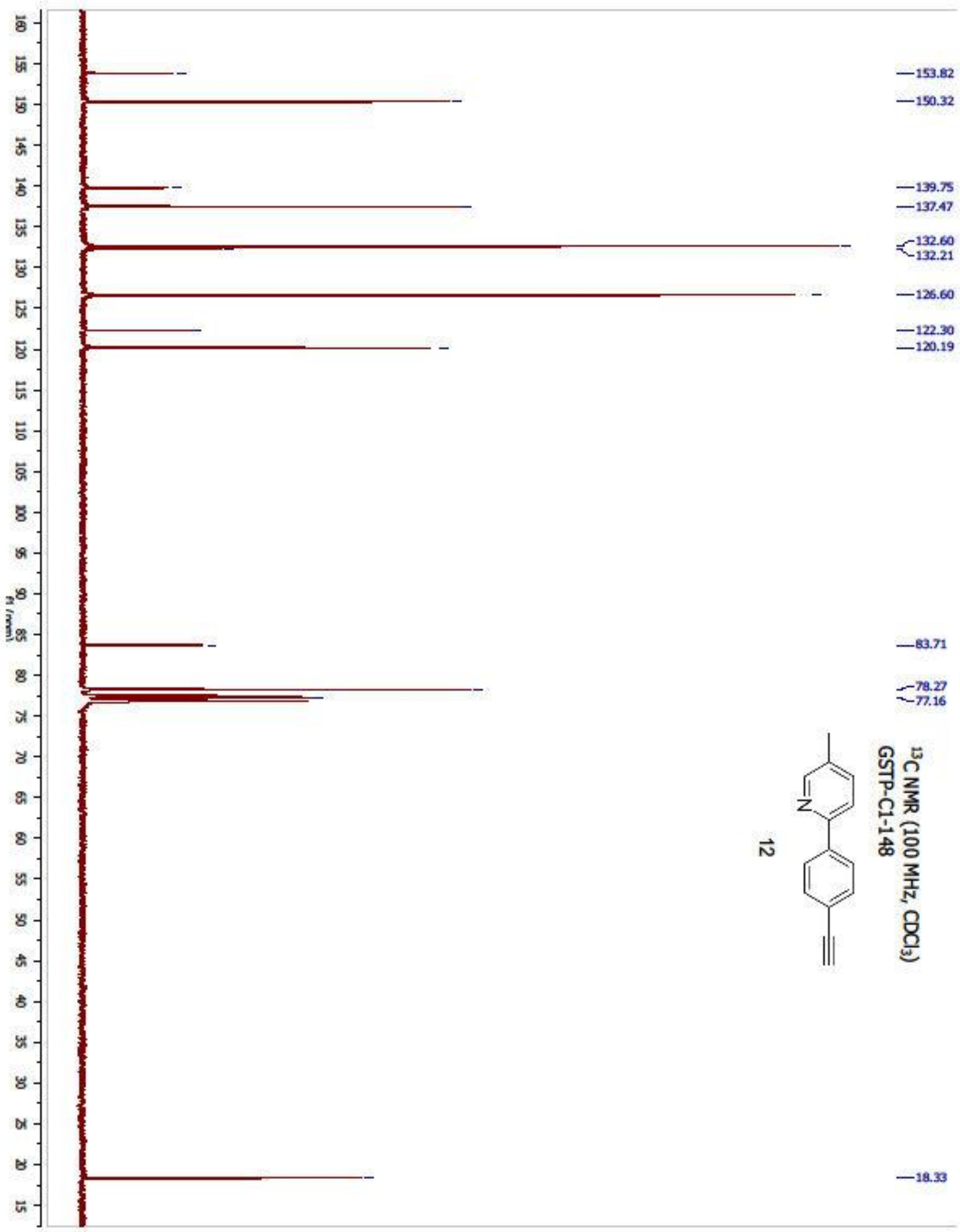
^{13}C NMR (100 MHz, $CDCl_3$)
GSTP-C1-146

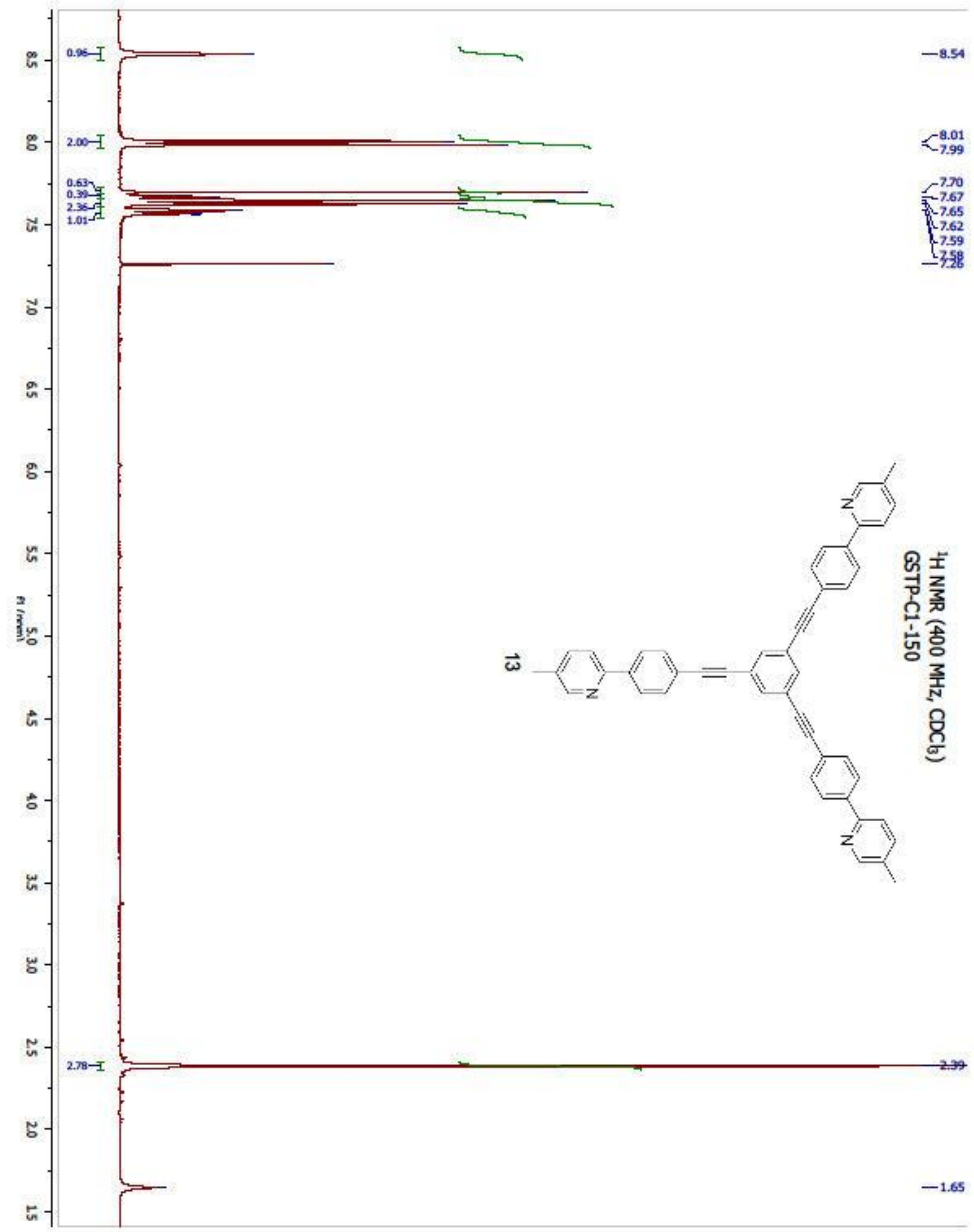
11

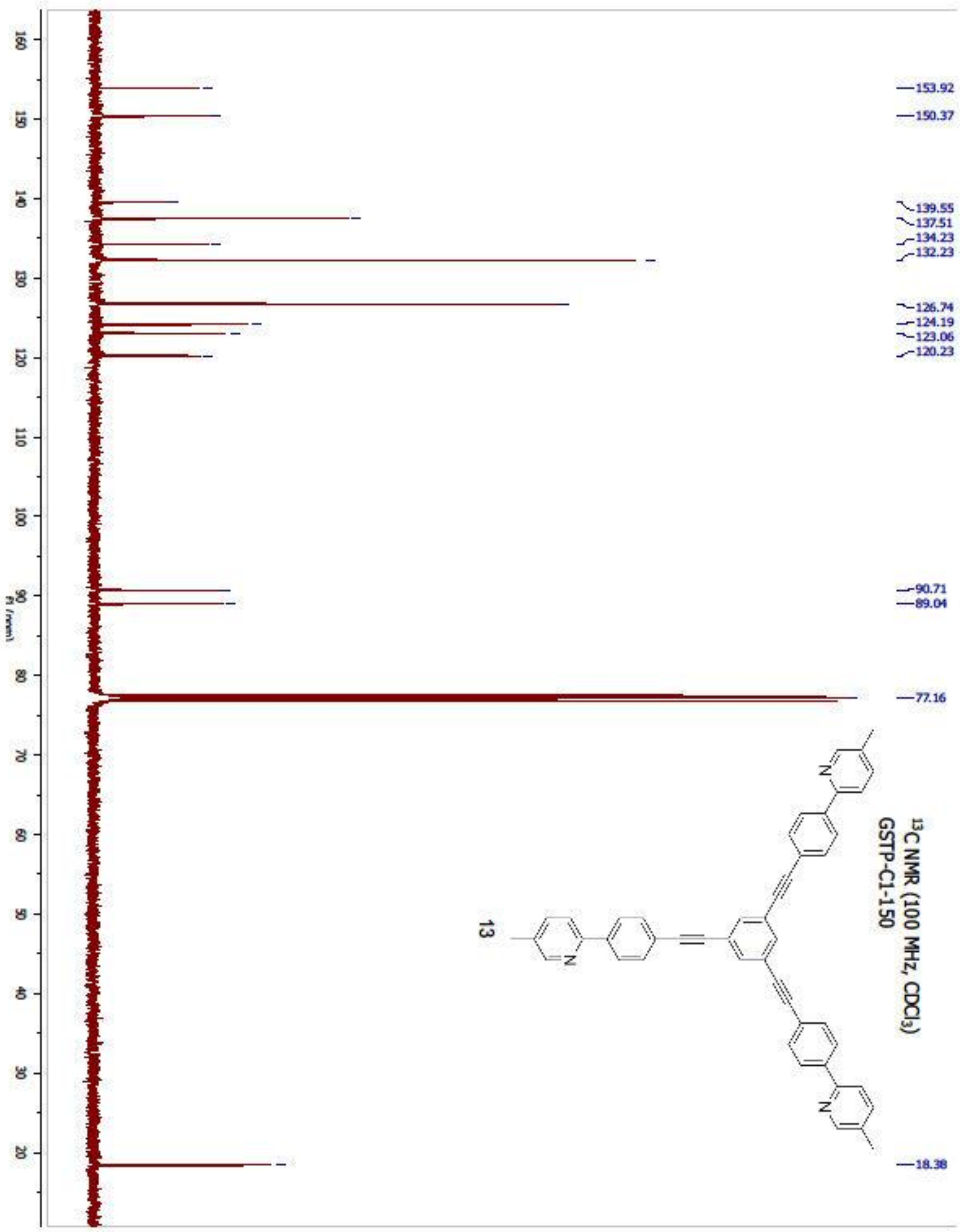


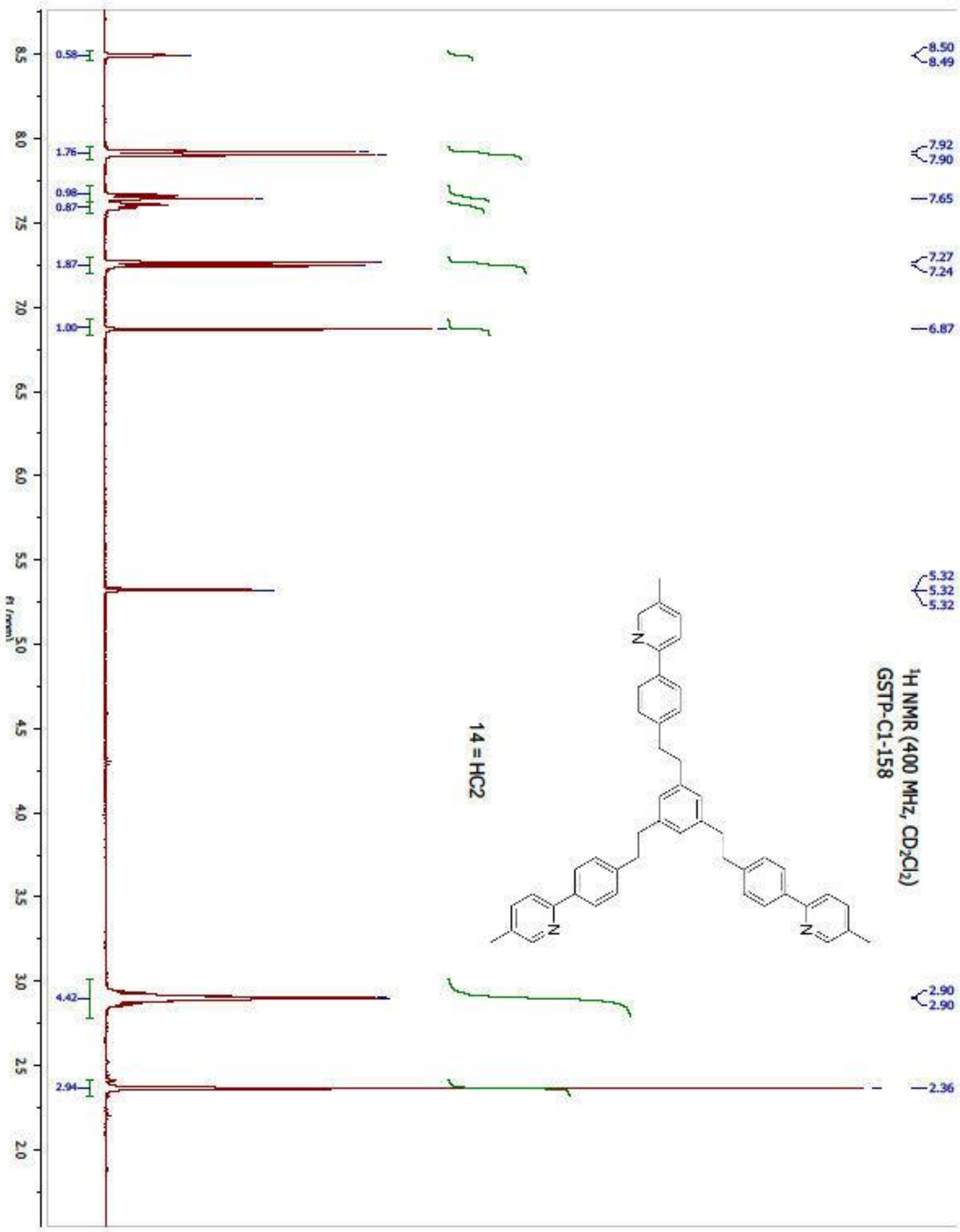
^{1}H NMR (300 MHz, $CDCl_3$)
GSTP-C1-148

12


^{13}C NMR (100 MHz, CDCl$_3$)
GSTP-C1-148
12
N
153.82
150.32
139.75
137.47
132.60
132.21
126.60
122.30
120.19
83.71
78.27
77.16
18.33
f1 (ppm)
160
155
150
145
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15

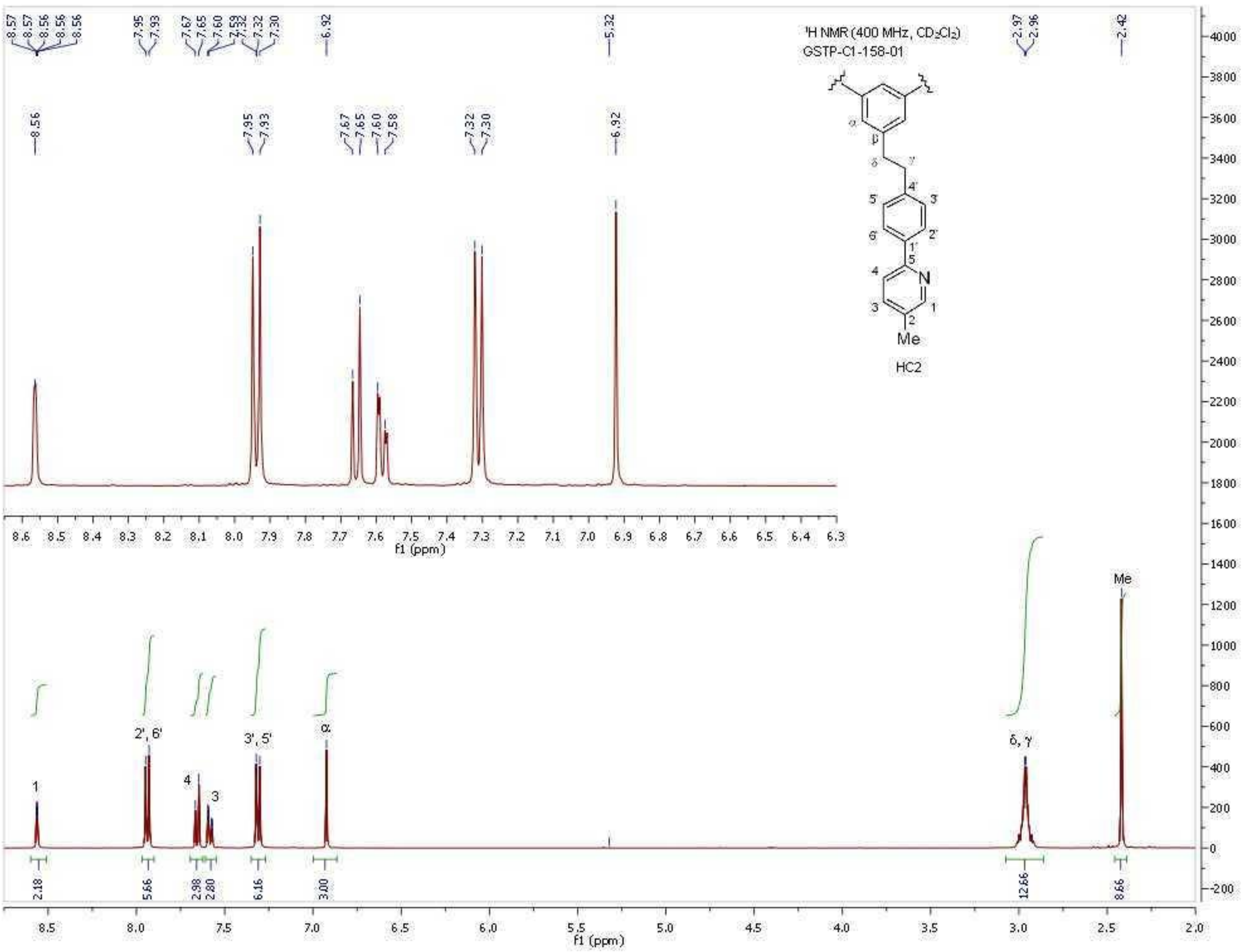

^{1}H NMR (400 MHz, CDCl$_3$)
GSTP-C1-150
13
N
N
N
8.54
8.01
7.99
7.70
7.67
7.65
7.62
7.59
7.58
7.26
2.39
1.65
0.96
2.00
0.63
0.39
2.36
1.01
2.78
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
f1 (ppm)

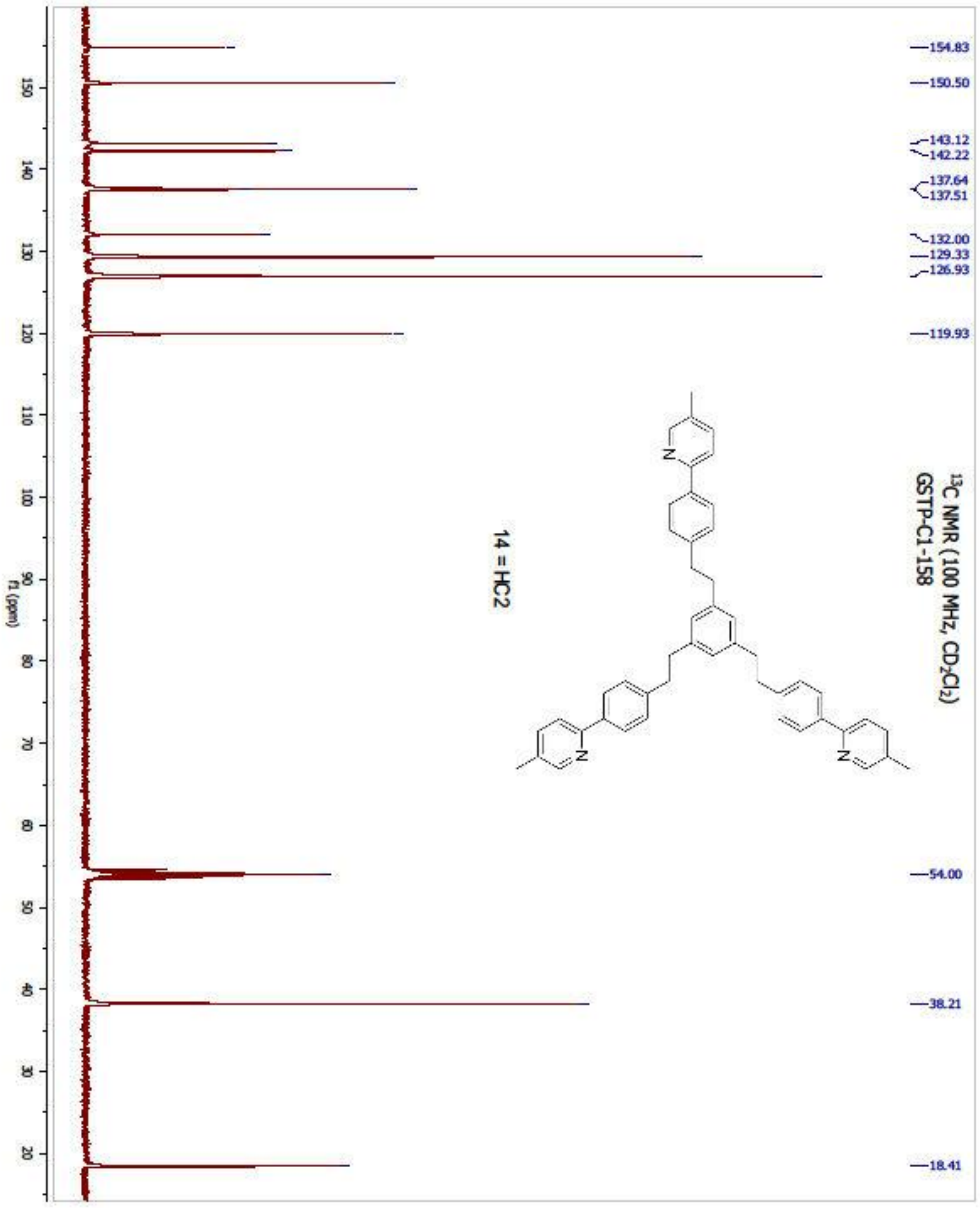

13C NMR (100 MHz, CDCl3)
GSTP-C1-150
13
153.92
150.37
139.55
137.51
134.23
132.23
126.74
124.19
123.06
120.23
90.71
89.04
77.16
18.38
f1 (ppm)
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
N

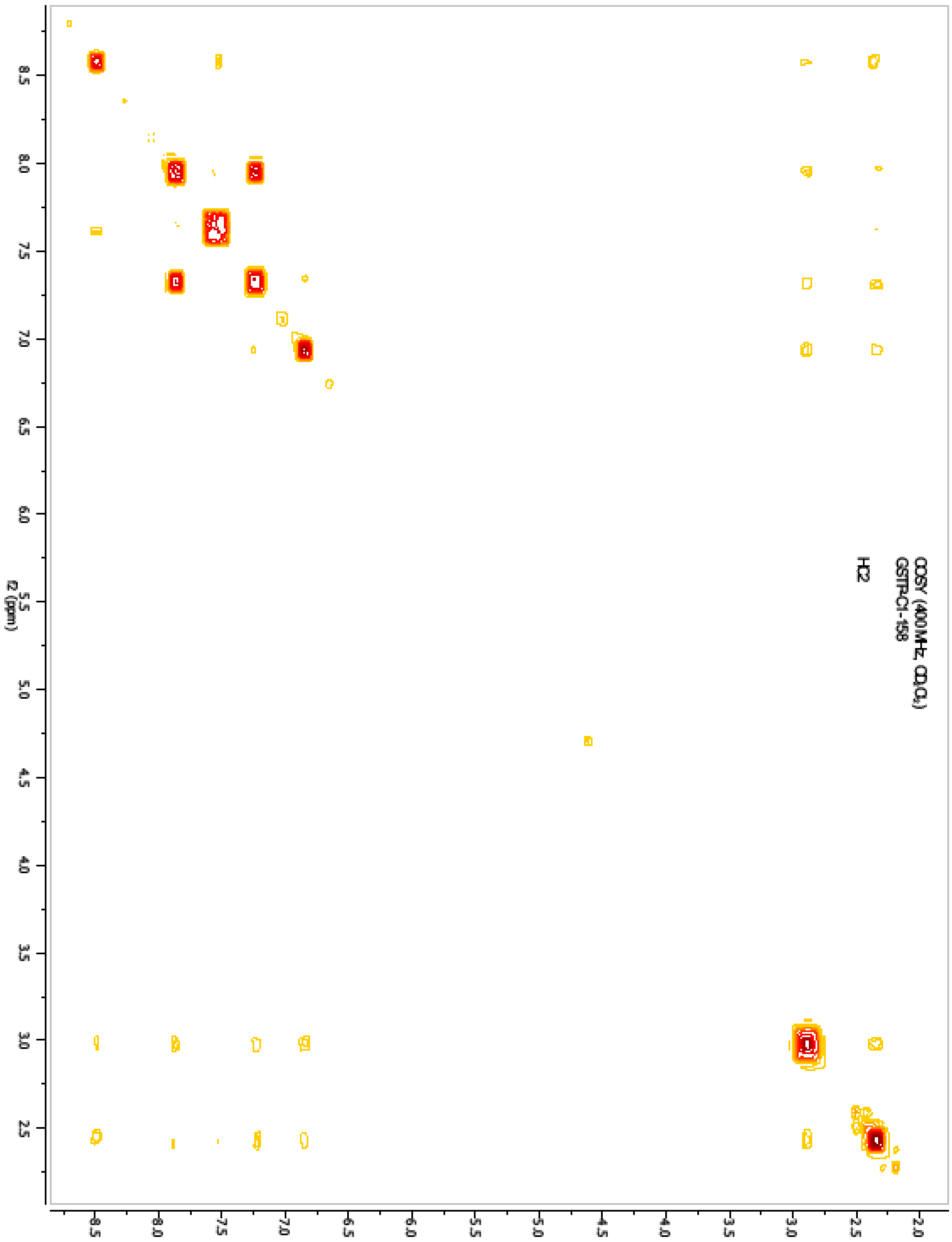


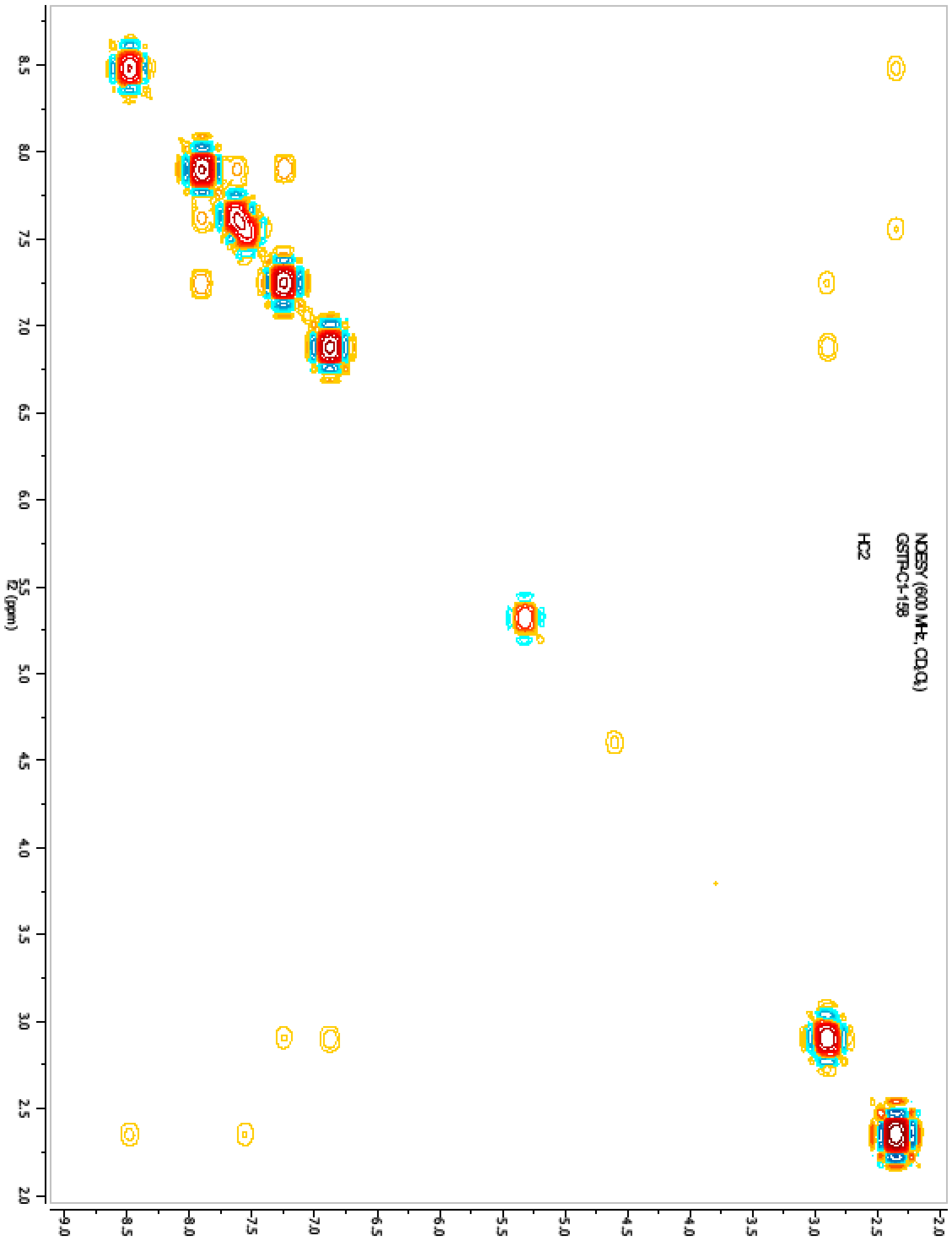
^{1}H NMR (400 MHz, CD_2Cl_2)
GSTP-C1-158

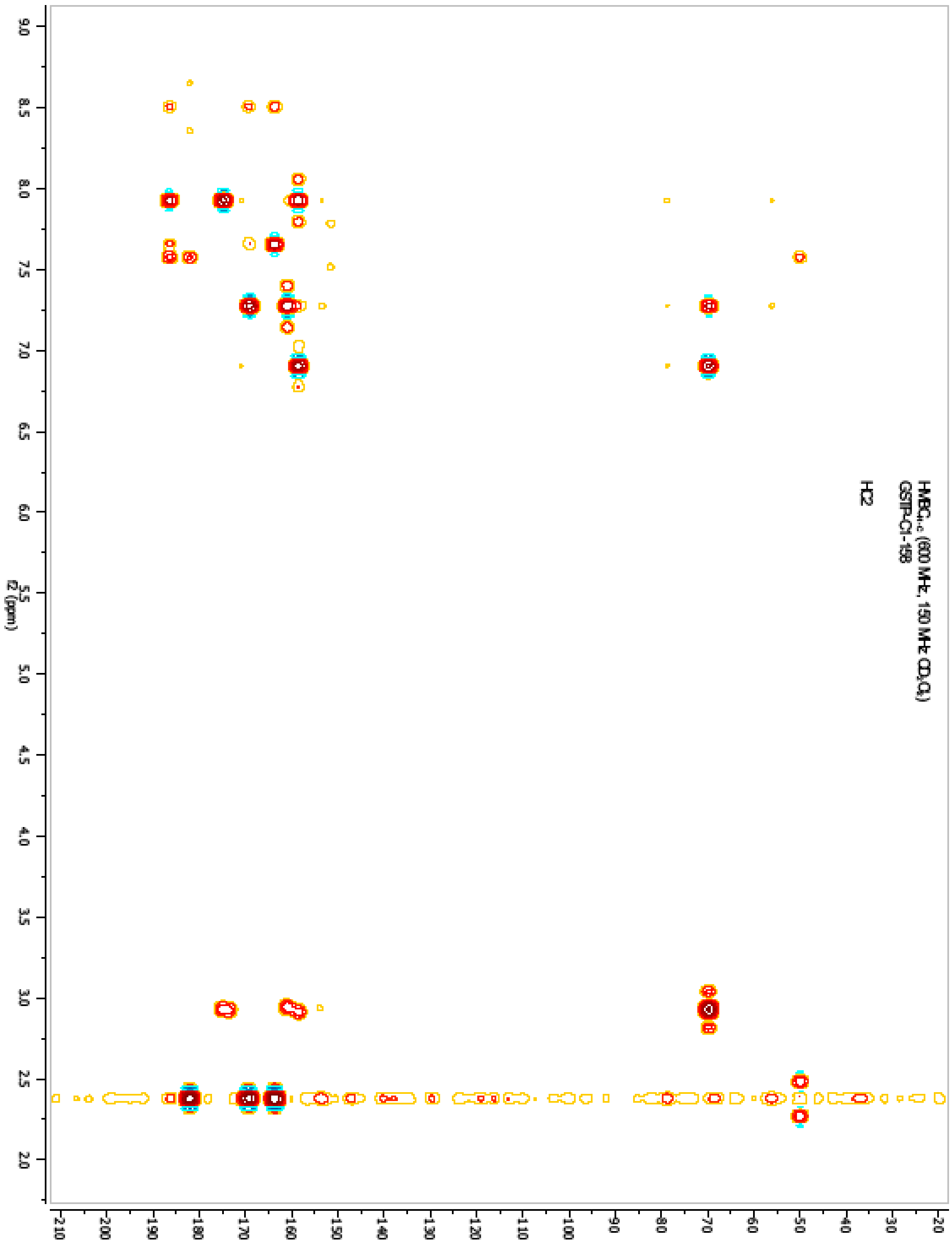
14 = HC2

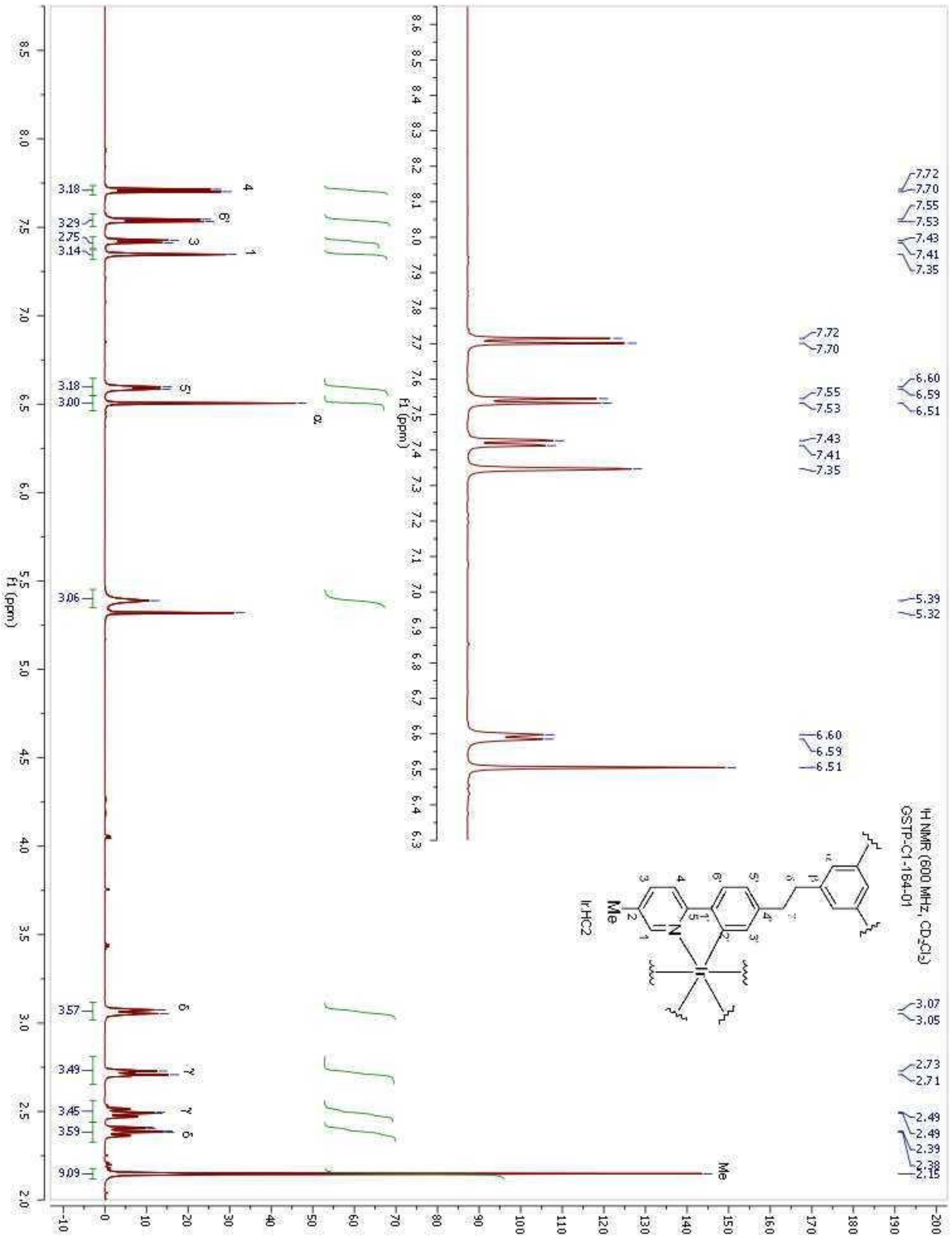

¹H NMR (400 MHz, CD₂Cl₂)
GSTP-C1-158-01
HC2
Me
N
α
β
γ
δ
1
2
3
4
5
1'
2'
3'
4'
5'
6'
8.57
8.57
8.56
8.56
8.56
7.95
7.93
7.67
7.65
7.60
7.59
7.32
7.32
7.30
6.92
5.32
2.97
2.96
2.42
8.56
7.95
7.93
7.67
7.65
7.60
7.58
7.32
7.30
6.92
f1 (ppm)
1
2', 6'
4
3
3', 5'
α
δ, γ
Me
2.18
5.66
2.98
2.80
6.16
3.00
12.66
8.66
f1 (ppm)

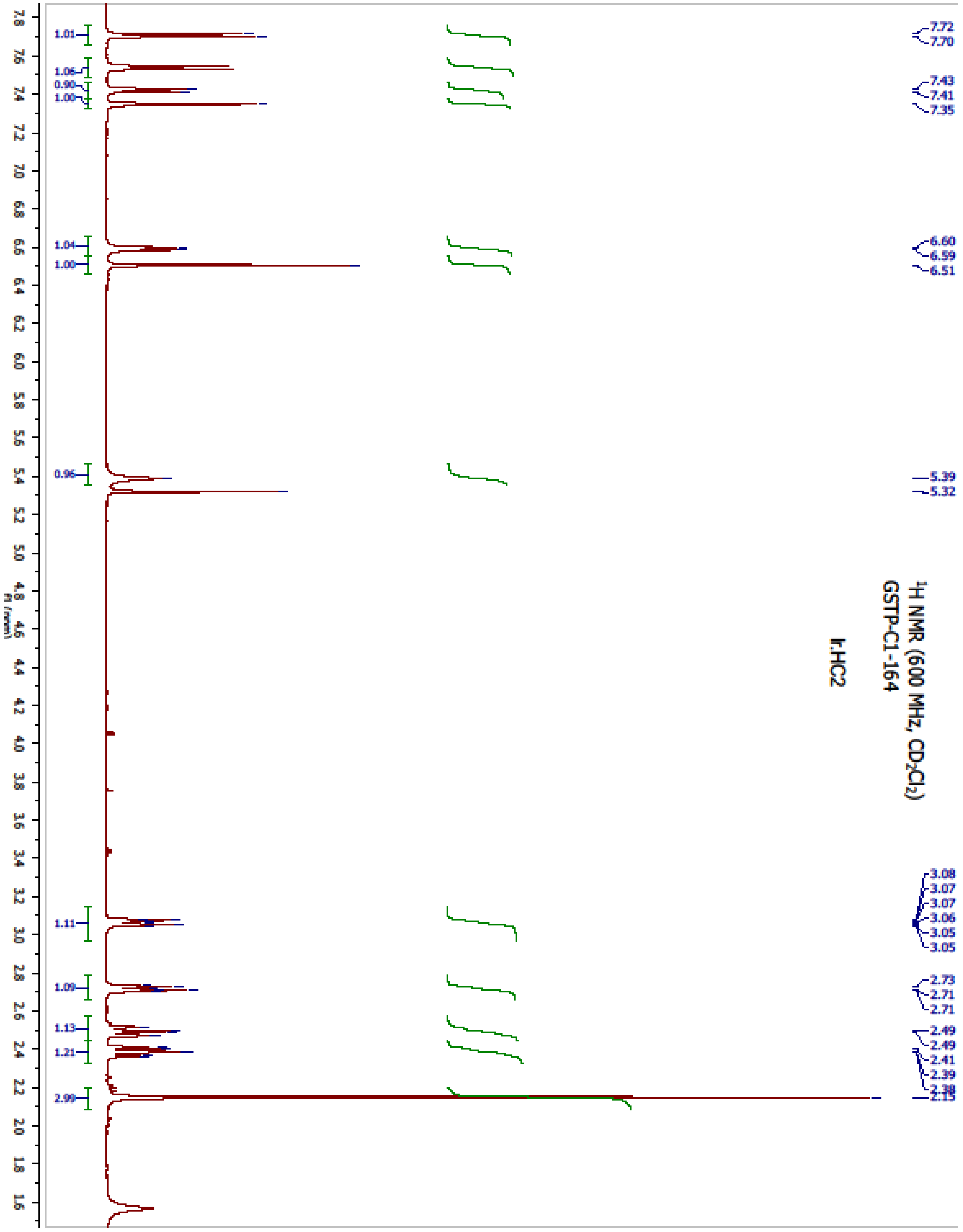

^{13}C NMR (100 MHz, CD_2Cl_2)
GSTP-C1-158
14 = HC2
N
N
N
154.83
150.50
143.12
142.22
137.64
137.51
132.00
129.33
126.93
119.93
54.00
38.21
18.41
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)

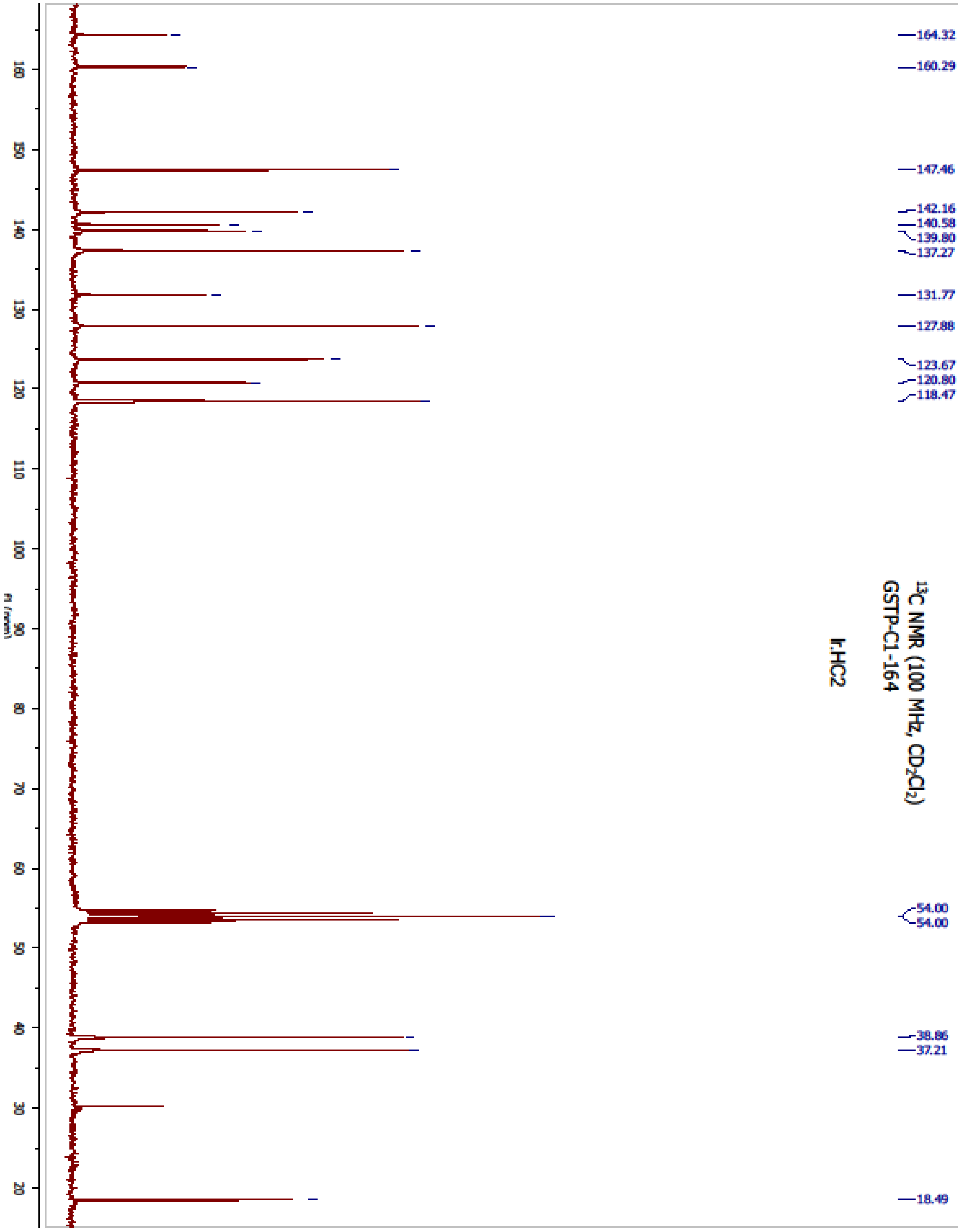

COSY (400 MHz, CD_2Cl_2)
GSTRC1-158
H2
f2 (ppm)
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0

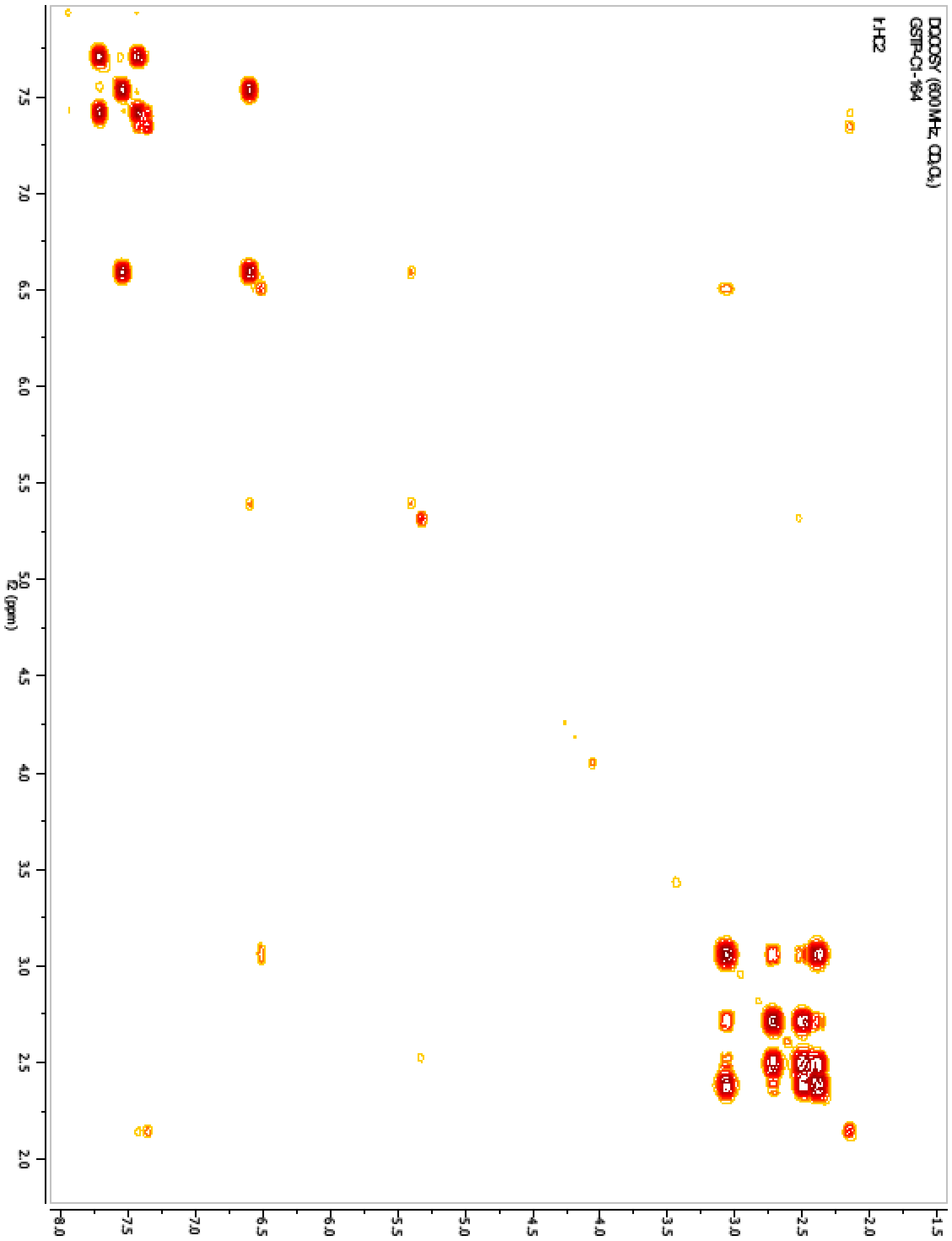

NOESY (600 MHz, CD2Cl2)
GSTPC1-158
HC2
f2 (ppm)
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0

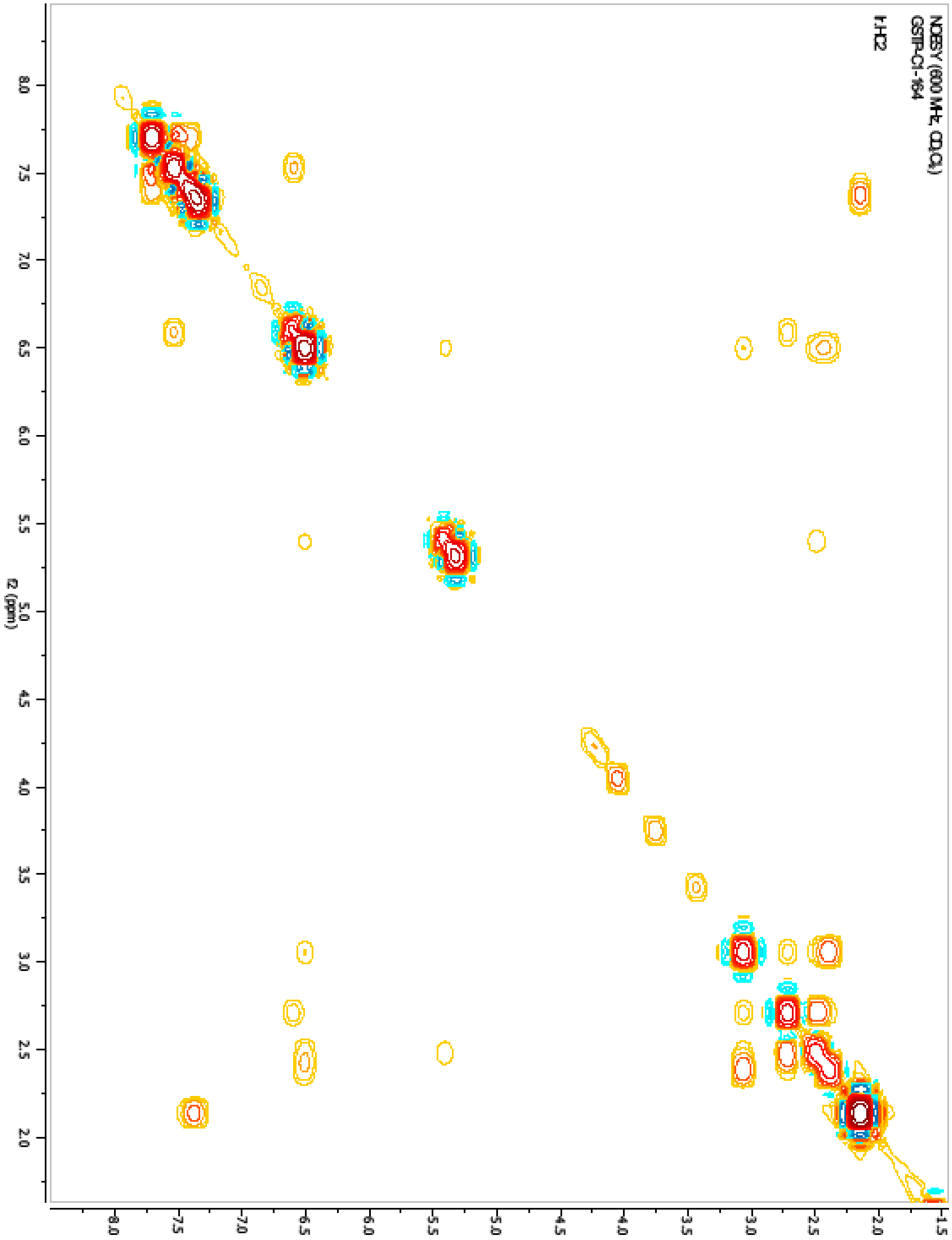

HMBC$_{H\text{-}C}$ (600 MHz, 150 MHz CD$_2$Cl$_2$)
GSTP-Cl-158
H2
f2 (ppm)
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20

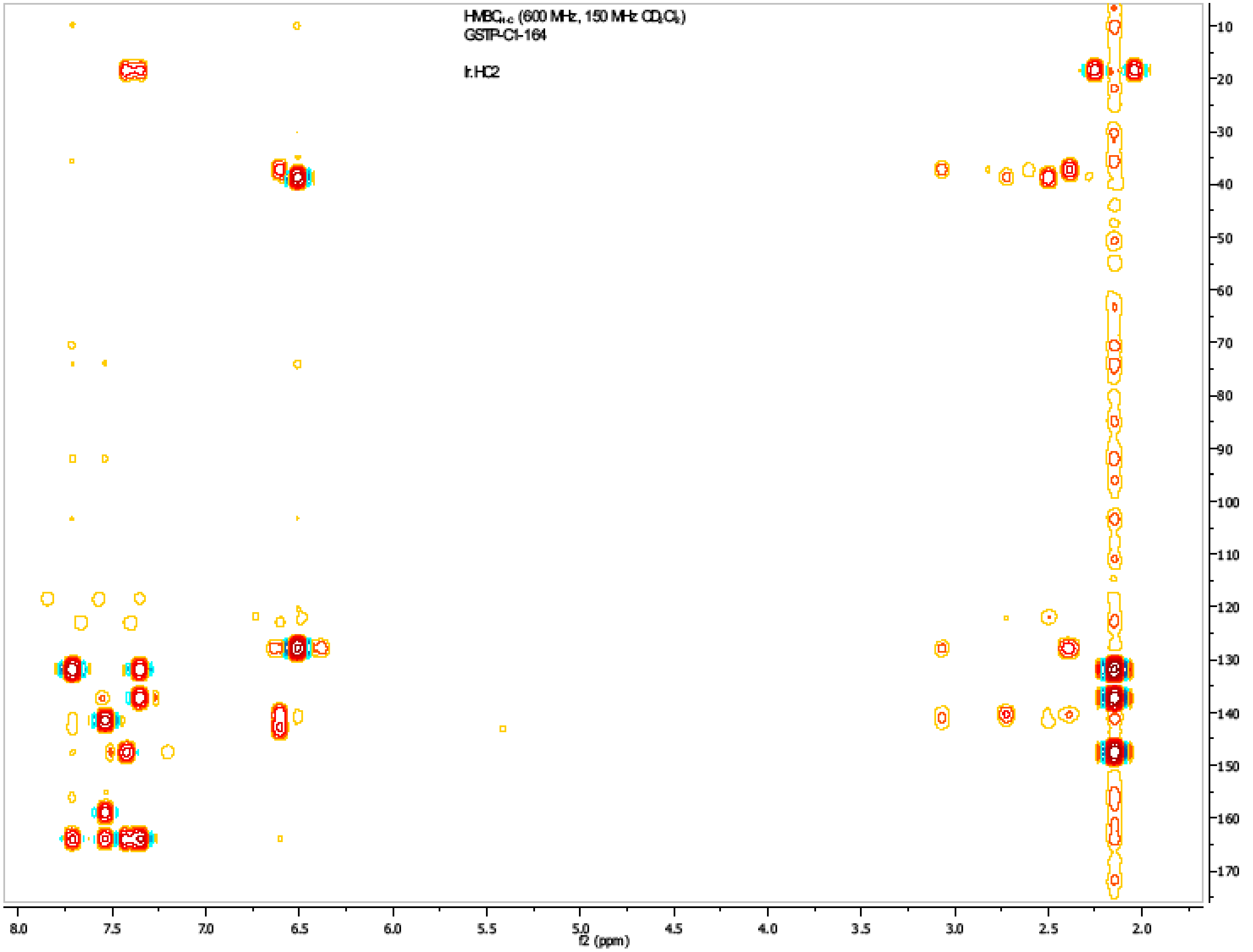

¹H NMR (600 MHz, CD₂Cl₂)
GSTP-C1-164-01
Ir.HC2
Me
f1 (ppm)
7.72
7.70
7.55
7.53
7.43
7.41
7.35
6.60
6.59
6.51
5.39
5.32
3.07
3.05
2.73
2.71
2.49
2.49
2.39
2.38
2.15
3.18
3.29
2.75
3.14
3.18
3.00
3.06
3.57
3.49
3.45
3.59
9.09
4
6'
3
1
5'
α
δ
γ
γ
δ
Me


1H NMR (600 MHz, CD2Cl2)
GSTP-C1-164
Ir.HC2
7.72
7.70
7.43
7.41
7.35
6.60
6.59
6.51
5.39
5.32
3.08
3.07
3.07
3.06
3.05
3.05
2.73
2.71
2.71
2.49
2.49
2.41
2.39
2.38
2.15
1.01
1.06
0.90
1.00
1.04
1.00
0.96
1.11
1.09
1.13
1.21
2.90
7.8
7.6
7.4
7.2
7.0
6.8
6.6
6.4
6.2
6.0
5.8
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
f1 (ppm)


^{13}C NMR (100 MHz, CD_2Cl_2)
GSTP-C1-164
Ir.HC2
164.32
160.29
147.46
142.16
140.58
139.80
137.27
131.77
127.88
123.67
120.80
118.47
54.00
54.00
38.86
37.21
18.49
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)


DQCOSY (600 MHz, CD_2Cl_2)
GSTP-C1-164
f1:H2
f2 (ppm)
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5


NOESY (600 MHz, CDCl3)
GSTP-C1-164
f1:H2
f2 (ppm)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5


HMBC$_{H-C}$ (600 MHz, 150 MHz CD$_2$Cl$_2$)
GSTP-Cl-164
Ir.HC2
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
f2 (ppm)
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170

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